

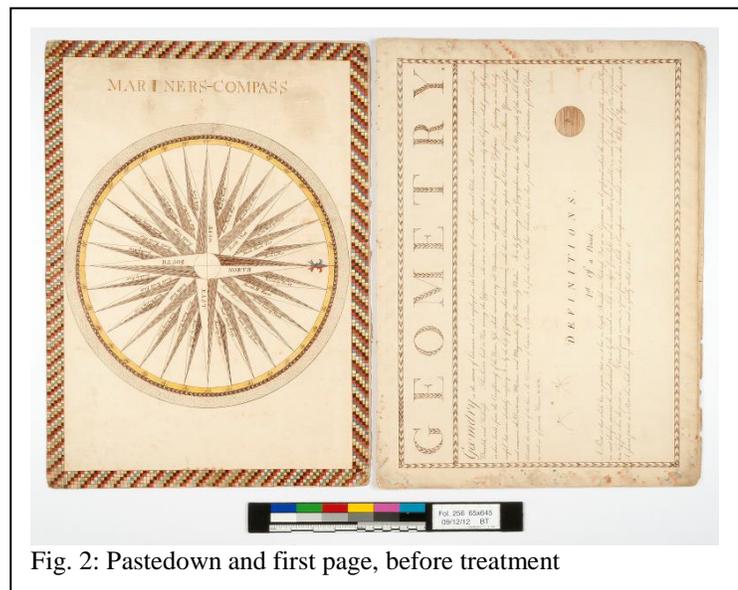
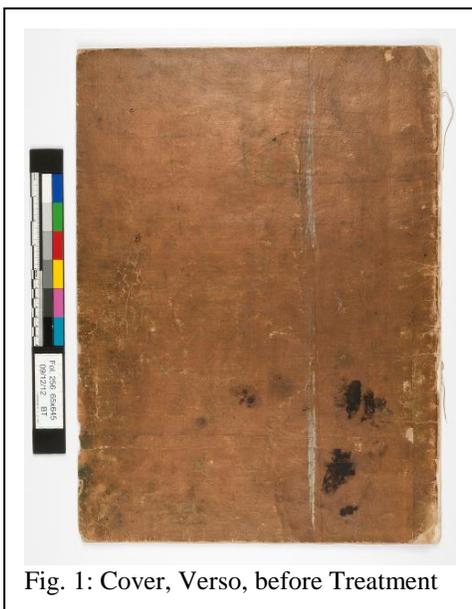
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**The Miscellaneous Works of Charles Barrell**

## ABSTRACT

*The Miscellaneous Works of Charles Barrell Ætatis 13: Performed at Mr. Wymans Boarding School in Medford 1797* is an early American manuscript in the Winterthur Museum, Garden, and Library's Joseph Downs Collection of Manuscripts and Ephemera. This exercise book, created by a 13 year-old boy, includes numerous geometry exercises and drawings, some of which are hand-colored. It is unusually large and is made from more expensive materials than similar manuscripts from this time period. The cover consists of several patches of a Dutch gilt paper, and the text block consists of full sheets of high-quality, handmade paper. The materials used are indicative of the Barrell family's social and economic status. Currently, no known technical analysis of this type of book has been conducted. The identification of the pigments and binders used for the hand-coloring and the Dutch gilt paper were the main focus of this study. The majority of the pigments detected were commonly used by artists in America during this time period, and the binding medium used was found to be gum Arabic. The metal used for the Dutch gilt paper was copper, but the binding medium for the metal could not be positively identified. The contents of the paper used for the text block were also of interest, because while the paper is not visibly blue, smalt was detected within the paper. Preliminary analysis was limited to examination using ultraviolet radiation, fiber identification, and X-Ray Fluorescence Spectroscopy (XRF). Further analysis was conducted using scanning electron microscopy (SEM), Fourier transform spectroscopy (FTIR), Raman spectroscopy, and gas chromatography-mass spectroscopy.



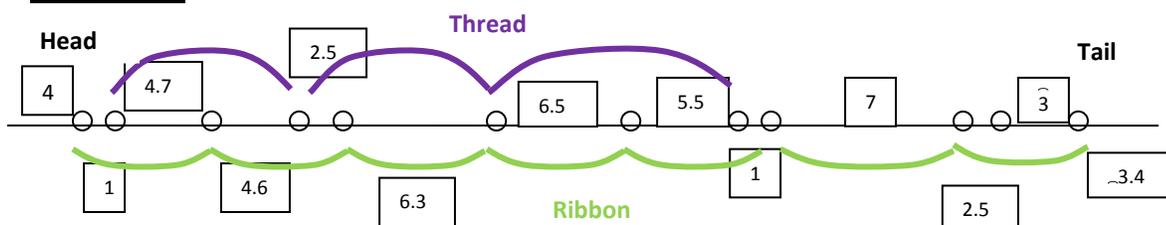
## 1. INTRODUCTION

*The Miscellaneous Works of Charles Barrell Ætatis 13: Performed at Mr. Wymans Boarding School in Medford 1797* is an early American manuscript in Winterthur's Joseph Downs Collection of Manuscripts and Ephemera. It was originally owned by the Winterthur Museum, Garden and Library, but was de-accessioned and added to the Joseph Downs Collection, which is a part of Winterthur's Library and contains a variety of primary documents, including manuscripts. Charles Barrell's book is one of over 60 mathematics exercise books in their collection, dating from the early 1700s to the late 1800s. Charles' book was brought to the conservation lab for treatment in preparation for an exhibition, and was chosen for technical analysis because it has a number of unique features; it is unusually large, is covered in several scraps of Dutch gilt paper, and has hand-applied coloring within the text block. As no known technical analysis of a similar manuscript has been conducted, it was hoped that details about the book's construction and use would be revealed through this study. A deeper understanding of the materials also proved helpful for interpreting the object and better understanding its preservation needs.

### 1.1 Description of Object

*The Miscellaneous Works of Charles Barrell* is a meticulously executed manuscript composed of six full sheets of handmade, laid paper which have been folded into a single folio. The outermost folio has been covered on the outside with scraps of Dutch gilt paper, which allows it to serve as a pastedown.<sup>1</sup> The sheets are attached by pamphlet sewing down the middle fold. This appears to have been done first using ribbon, but was later repaired using thread. Some of the original sewing holes were reused and new holes were made. Both the old and new holes, as well as the placement of both the new and old sewing materials are shown below in Diagram 1.

**Diagram 1<sup>2</sup>**



<sup>1</sup> A pastedown is: "The plain, colored, fancy, or marbled paper attached to the inside of the board of a book after it has been covered, or when it is cased-in (Etherington and Roberts, 2011)."

<sup>2</sup> All measurements are in centimeters, and indicate the distances between holes, with the exception of the first and last measurements, which indicate the distances of the first and last holes from the edges.

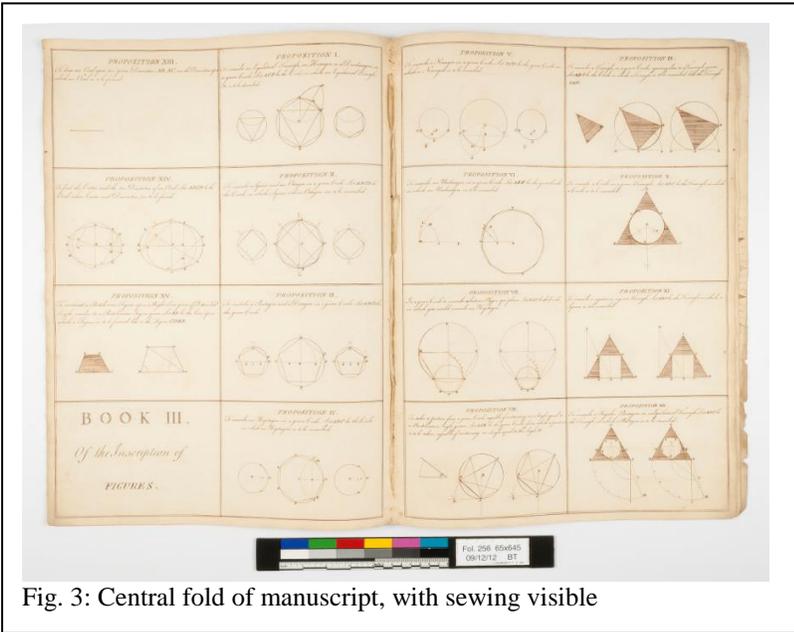


Fig. 3: Central fold of manuscript, with sewing visible

The text block consists of full sheets of medium-weight, off-white, handmade laid paper. No deckle edge is visible, which suggests the paper was trimmed. A crown and shield watermark is present, and has a fleur-de-lis inside as well as the letter “B” and a “JB” and “1795” below the shield. The countermark reads “Budgen/1795,” which indicates that this paper was likely produced

in England by Thomas Budgen and was imported to America (Shorter 1957). Please see Appendix A for images of the watermark. All of the pages are oriented in the same direction. The outer pastedown folio appears to consist of the same paper as the rest of the book. The paper is lightly sized, likely with gelatin based on the time period.

The majority of the manuscript is written using iron-gall ink.<sup>3</sup> The first page is titled “Geometry” and the majority of the manuscript is divided into five “Books”, which all refer to geometry, but there is no table of contents. Many of the pages have two columns, each of which is divided into four boxes. The sections generally follow a sequence like that of a newspaper; the text begins in the upper left box, and should be followed down the left column then up to the top of the right column. The handwriting and figures were carefully and precisely copied. Lines inscribed using drawing aids such as straight-edges and compasses are clearly visible, as well as small holes from compass points. The final pages of the book are filled with illustrations.

There are four pages which exhibit hand-applied color, including a full-page map, entitled “The World/ enlarged/ from the Encyclopedia,” and a page with drawings of flowers, located at the back of the manuscript. Numerous colors were applied to these pages, including varieties of green, yellow, blue, and red. The front pastedown displays a drawing of a large “Mariners-Compass” and is surrounded by a checkered border of blue, red, yellow, and black-brown, and empty (or white) squares. The back pastedown displays the creator’s colophon, which is contained in an elliptical border surrounded by ray-like, hand-colored designs in various shades of red and yellow.

<sup>3</sup> This was determined through both visual identification and the use of X-ray fluorescence spectroscopy (XRF).

## 1.2 Condition Summary

Overall the manuscript is in good condition. While the pages exhibit some minor areas of staining and discoloration around the edges, they are remarkably intact. The sewing has failed and the cover has split in half down the fold, and as a result the cover is detached from the book. While both the original sewing and the first campaign of repair sewing are no longer intact, both the silk ribbon from the original sewing and the thread from the repair attempt are still present in the center of the folio.<sup>4</sup> The silk ribbon is visibly brittle and discolored.

The Dutch gilt paper on the covers is in poor condition. While the former embossed design is faintly visible in some small areas, it has been abraded away from the majority of the surface. Numerous scratches, creases, losses, stains, and accretions are also present on both the front and back covers. It was likely a more colorful and metallic surface originally, but due to damage from abrasion and handling the cover now appears to be an uneven, slightly metallic bronze color. There are several areas of green corrosion on both of the covers.<sup>5</sup> There is a larger area of loss on the bottom of the front cover, shown in Figure 4, which was likely caused or accelerated by the same water event that created tidelines on the folio pages (See description below).

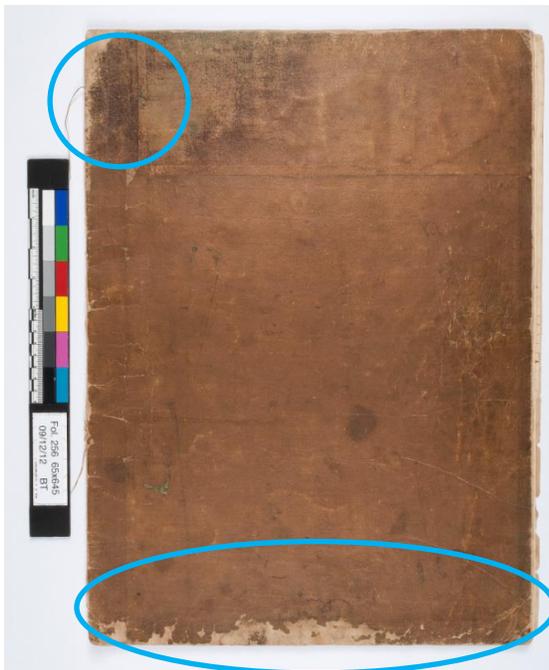


Figure 4: Front cover showing damage. Blue indicates major losses.

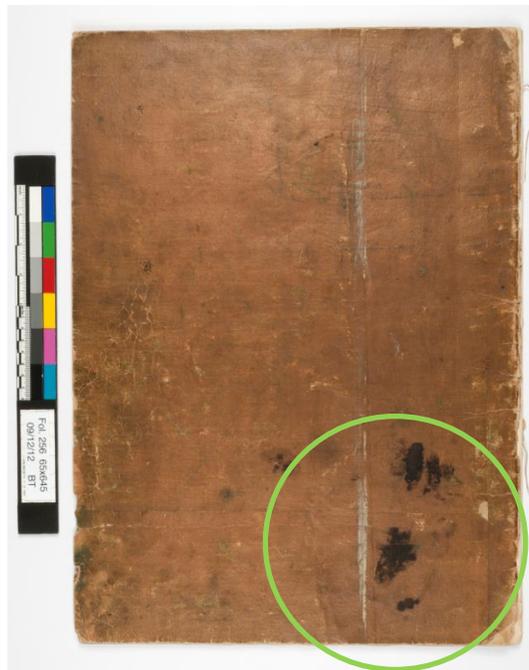


Fig. 5: Back cover showing damage. Green indicates major accretions.

<sup>4</sup> Please refer to the fiber identification section for more information regarding how the fibers were identified.

<sup>5</sup> Little research is available related to Dutch gilt paper, and this will be addressed further in section 1.6. It is not known if corrosion is a common condition issue among gilt papers.

There is a significant amount of dirt in the gutter of the folio. The pastedowns exhibit more dirt and abrasion than the pages of the text block, and the edges of each page exhibit brown discoloration. Areas of abrasion as well as some slight tears are also visible along the edges of several pages. Strike-through from the iron gall ink is visible on almost every page, but the ink is in excellent condition overall. Small amounts of foxing are also present on a majority of the pages. The colored inks from the decorated front pastedown have offset onto the first page in approximately 30% of the marginal area. Highly visible tidelines are present along the bottom edge of the first page, the last two pages, and the loose page in the back. Faint tidelines are slightly visible on the remainder of the pages in the same location. This was likely the result of a water event.

### **1.3 A Short survey of American ciphering books in Winterthur's Joseph Downs Collection**

The Joseph Downs Collection is part of the Winterthur Library, and contains a collection of manuscripts and ephemera related to American material culture. Their collection contains over 50 exercise books related to mathematics education in early America. As there is little scholarship currently available related to the use and composition of this type of manuscript, a short survey of the mathematics exercise books in the Downs collection was conducted. Approximately 26 math exercise books from between 1765 and 1820 were examined, so that Charles Barrell's book could be placed within a broader cultural context. These books were selected based on their approximate dates. This allowed for more informed decisions regarding what aspects of the book should be further examined and analyzed. *Please refer to Appendix B for a list of the manuscripts examined.*

Copybooks are generally defined as handwriting exercise books, while mathematics exercise books are called ciphering books. The term ciphering refers to a specific method of arithmetic which existed for centuries and was brought to America from Europe. Because these objects have rarely been studied, there is no standard terminology within library and archive collections, so these terms are often used interchangeably. The term mathematics exercise book is used in this paper, because while Charles Barrell's book was made in accordance with the ciphering tradition, it does not contain ciphering. The few studies of this type of manuscript focus on the history of math education, rather than material composition, which is why this survey was essential.

Overall, it was found that the format chosen for Charles' book was not uncommon. Of the 26 books examined, 10 were single section folios. Of these, 14 had paper covers. Out of all of the math exercise books in the Downs collection, only one other is similar in size to Charles Barrell's book; most are 33 cm tall or shorter and are more rectangular in shape. Ribbons were not used as a sewing material for any of the books examined. Most of the books contained ciphering, and only 4 of the books contain geometry exercises like Charles' book. This is not surprising, because at the time it was unusual for students to learn math in school, and geometry was taught even more infrequently, often only to more advanced students or to those who were planning to enter careers related to navigation or surveying (Clements and Ellerton 2012).

It is also fairly common to see flourishes and fancy headings within the books. This was done purposefully, because writing and math were often taught together and the flourishes served to show the students handwriting abilities (Clements and Ellerton 2012). Some students went above and beyond in displaying their handwriting skills; 15 of the books surveyed included marginalia of some kind, and 10 of these included hand-coloring. Birds, faces, and flowers were fairly common, and illustrations are sometimes incorporated into the exercises.

Based on the comparative examples examined in this survey, it must be concluded that Charles Barrell's book is unusual. It is larger than average, and is made from uncommon materials, including Dutch gilt paper and a blue silk ribbon. His book is comparatively meticulous and thoughtfully planned, which suggests its intended use as presentation of his best work. The fact that Charles was learning geometry also sets him apart from the average student.

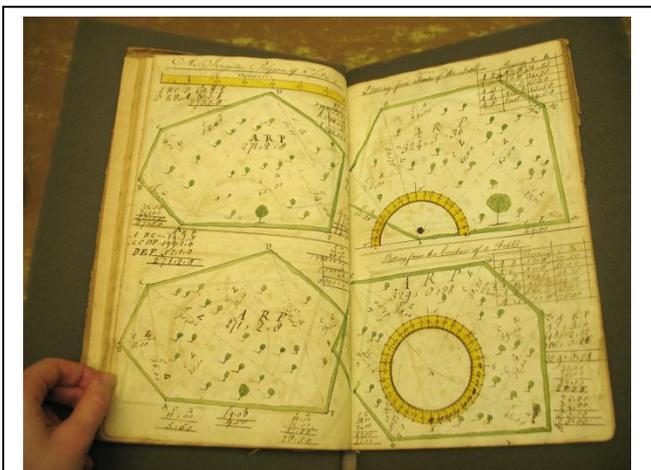


Fig. 6: Comparative example from the Downs Collection, book of W. Bordman (1774)

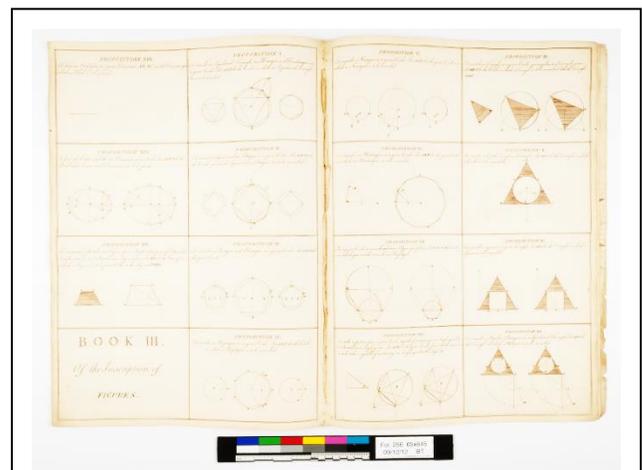


Fig. 7: Comparative image of Charles Barrell's book (1797)

### **1.5 History of Education in Late 18<sup>th</sup> century America and Mr. Wyman's Boarding School**

During this time period, penmanship was considered a separate discipline from literacy, and many people who were able to read had not been trained in fine handwriting (Nash 1969). Boston was the center of academic training in America, and its handwriting experts and pupils were envied, although the teaching of penmanship was becoming increasingly more common thanks to newly published handwriting manuals (Nash 1969).

It is important to note that ciphering books were used differently from notebooks are used in schools today. They were not made for practice or while taking notes quickly in class; the problems would have first been done on a slate, and when the student solved the problem correctly, they were allowed to enter it into their book (Clements and Ellerton 2012). In the absence of standardized tests, these served as a record of the students education, and as proof of their teacher's abilities (Clements and Ellerton 2012). They would have been presented like portfolios, to colleges or employers. Most of these books were made by 13 or 14 year olds, who were hoping to attend college soon. These would have also served the student as a reference manual for their entire life, because while printed textbooks were available, they were still relatively scarce (Clements and Ellerton 2012).

According to the colophon on the back pastedown of the book, Charles completed this book at "Mr. Wyman's Boarding School in 1797." However, it is suspected that Charles was not trained entirely at Mr. Wyman's Boarding School in Medford, Massachusetts. A record of the history of Medford mentions a Mr. Wyman's boarding school on High St. in Medford, Massachusetts, now near Tufts University. This school consisted of both public and boarding schools, and included institutions for both boys and girls. Mr. Wyman's school was short lived; he opened it in 1795, and he was replaced in 1800 by Susanna Rowson (Hooper 1906). This suggests that Charles Barrell could not have completed the entirety of his education at Mr. Wyman's school. In 1797, at age 13, he could only have been at the school for two years at the time this book was produced. It is unlikely that he would have stayed at Mr. Wyman's for much longer, given that many boys began college at age 14 during this time period (Doar 2006; Clements and Ellerton 2012).

#### **1.4 History of Joseph Barrell and the Barrell Family**

Almost no information is available regarding how this object arrived at Winterthur, who its previous owners were, and what became of the book's creator, Charles Barrell. Though this book is currently considered part of the Downs Collection, it was once a museum object and was kept in the Winterthur Museum in the drawer of a desk which belonged to the Barrell Family (Fol. 256). The majority of the history of this object's original owner may be found in the museum record for the desk (53. 56.23 Desk and Bookcase).

The recorded history of the Barrell Family is largely the history of Charles' father, Joseph Barrell. Joseph Barrell was a prosperous Boston merchant, who was personal friends with John Adams and Charles Bulfinch, the famed architect. Bulfinch had in fact worked for Barrell in his younger years, before traveling to Europe and training to be an architect, and later designed the Barrell family's mansion, named Pleasant Hill (Fales 1960). Joseph spared no expense in furnishing the mansion, which was filled with high quality furnishings, many of which were imported (Fales 1960). This suggests that the materials used for Charles' book, which include Dutch gilt paper, artists pigments, and large sheets of expensive paper, would not have been a financial burden for Charles' family, and are likely indicative of Charles' social and economic status. It also suggests that there may have been high standards for Charles' performance in school and high expectations for his adult life.

#### **1.6 Review of literature and related studies**

The composition of the Dutch gilt paper, including any pigments, metal particles, and binder present, were investigated in the hope of revealing information related to its method of construction. Gilt papers were only manufactured in Germany and Italy (Pezzati 2004). It is known that both wood blocks and copperplates were used to attach gold, silver, and copper leaf to colored paste paper, and the adhesive material used included animal glue, talc, and gums (Loring 1952; Wolfe 2008, 145-149). While this paper was only manufactured in certain parts of Europe, it was available and used to cover books in America during the late 18<sup>th</sup> Century (Loring 1952,53). No known technical analysis of Dutch gilt paper is currently available in the English-speaking world. The Arbeitskreis Buntpapier (Working Group of Colored Paper), a German group of museum and library professionals, has been conducting research related to the manufacture of Dutch gilt paper, but as their research is still ongoing and in German, it is not particularly accessible (buntpapier.org November 30, 2012).

Studies relating to the use of pigments on works of art on paper during this time period are limited. The materials used for hand-coloring were likely similar to those used for other works of art on paper in colonial America, such as fraktur and watercolor, because colorants were generally imported from Europe (Harley 1970). A number of studies of fraktur have been conducted at Winterthur, much of which has not been published. In 1978 John Krill and Janice Carlson were the first to use X-Ray Fluorescence Spectroscopy (XRF) to analyze fraktur (Krill and Carlson 1978). They did not use any other analytical techniques in addition to XRF, because non-destructive analysis was desired (Krill and Carlson 1978). Currently, while XRF continues to play an important role in the analysis of pigments on paper, Raman spectroscopy may also be used for non-destructive analysis (Bescoby, et. al. 2007). In 2005, a significant amount of research was done in preparation for the exhibition *Making Fancy: Materials and Methods in Pennsylvania German Fraktur* at Winterthur. The unpublished exhibit plaques address contemporary analytical techniques, which include XRF, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and gas chromatography-mass spectrometry (GC-MS). These additional techniques are logical compliments to XRF. While XRF provided information about the elements present using non-destructive means, Raman provided information about the molecular compositions of the materials, and FTIR and GC-MS provided information about the binding media.

Research regarding watercolors used in America at the end of the 18<sup>th</sup> century has largely addressed studies of trade catalogues, artist's manuals, and available artist's palettes (Krill 1992). While the materials addressed in these studies of fraktur may be similar to those found in Charles Barrell's book, some unanswered questions remain. The resources available to creators of fraktur, who presumably lived in rural Pennsylvania, may have differed from the resources available to Charles Barrell, who was the son of a wealthy merchant in Boston.

The contents of the paper used for the text block were also of interest, because the presence of smalt was detected (See the Results and Discussion sections of this paper). The use of smalt to make yellow paper fibers appear whiter, like modern optical brighteners, is recorded in a number of sources (Brückle 1993, Perkinson 1997, Krill 2002). In his 2002 book *English Artist's Papers*, John Krill documented the presence of smalt used as "blueing" in paper using scanning electron microscopy (SEM), but only includes a back scatter election image (BSE). He also includes energy dispersive x-ray fluorescence data (EDS), which indicates that silicon, cobalt, and arsenic were detected within his fiber sample (2002, 145).

## 1.7 Technical analysis

The findings of this investigation helped to further define object's historical context. The two main areas of interest for this study were the Dutch gilt paper and the hand-colored drawings. The major goal was to classify and identify the materials present, because no known literature has been published related to trends in the materials used to create late 18<sup>th</sup> and early 19<sup>th</sup> century American copybooks or ciphering books. The composition of the Dutch gilt paper was of interest, including any pigments, metal particles, and binder present. It was hoped that analysis of the components of the Dutch gilt paper might reveal information related to its method of manufacture. The pigments and binders used in the hand-colored areas were also analyzed and compared to materials which were known to have been used by artists in the late 1700s. While the hand-applied colorants appear visually similar to watercolors, the binding medium using was not known for certain. The third area of interest in this study was the characterization and documentation of smalt in the text block paper.

## 1. EXPERIMENTAL

In conducting this research, non-destructive analysis was relied upon as much as possible, as was done in the British Museum's study of the John White watercolors (Bescoby 2007). The analytical techniques initially used included fiber identification, examination using ultraviolet radiation, and XRF. Further analysis using Raman, Scanning Electron Microscopy (SEM), FTIR, and GC-MS was conducted in order to elaborate on the initial findings. For SEM, both back scatter election image (BSE) and energy dispersive x-ray fluorescence data (EDS) were used.

### 2.1 Fiber Identification

In order to confirm the fiber contents of the paper and the sewing materials, samples were taken from the cover paper, the text block paper, and both of the sewing materials, including the ribbon and thread. A Wild Heerburg M8 microscope with Nikon 10x/23 ocular lenses and a FOSTEC Comet, EKE dual-gooseneck reflected light source was used to collect samples from all areas. A Nikon Labphot2-Pol- polarizing light microscope with Nikon CFWN 10x/20 CM oculars was then used to examine the samples. The samples were examined using the 10x, 20x, and 40X objectives, with both transmitted and polarized light. *Please refer to Appendix C for all sample locations.*

## 2.2 Examination using Ultraviolet Radiation

Examination in ultraviolet radiation (UV) was conducted using a UVP Model UVL-56 Blak-Ray Lamp with Long Wave UV (365 nm), operating at 115 V, 50/60 Hz, and 0.16 amps. This was done in order to further characterize the pigments, adhesives, and stains present. Fluorescence, or of lack of fluorescence, could reveal if certain pigments may be present and if repairs or attachment with certain adhesives were made.

## 2.3 X-Ray Fluorescence Spectroscopy

X-Ray Fluorescence (XRF) was chosen as a preliminary technique because it is capable of collecting data related to the elemental composition of an object, and can therefore help classify a multitude of inorganic materials. This made XRF a helpful first step in identifying pigments. An ArtTAX  $\mu$ XRF spectrometer equipped with a rhodium tube was used. The instrument specifications included a 600  $\mu$ A current, 50 kV voltage, and a 100 second collection time. The sample size allowed by the instrument is approximately 70-100  $\mu$ m. ArtTAX computer software was used. Due to the location of the hand-colored flowers on the page 18, the removal of any material would be highly noticeable. Because of this, only XRF was used to analyze the pigment used for the flowers. These colors may be compared to those found on the pastedown, which were analyzed using destructive methods. XRF was also used to analyze the composition of the Dutch gilt paper on the cover, the composition of the ink, and, inadvertently, the composition of the text block paper. *Please refer to Appendix C for all sample locations.*

## 2.4 Raman Spectroscopy

Raman can be used to identify both inorganic and organic pigments and grounds, and was therefore also used to acquire data related to the colorants within the manuscript. A Renishaw inVia Raman spectrometer with a 785 nm diode laser and 514 nm argon laser with spectral range 100-3200  $\text{cm}^{-1}$  was used. Both the 785 nm laser and 514 nm lasers were tested, but only the 785 nm laser was found to be successful. Only 0.1-10% of the laser power was used, and each sample location was scanned approximately 1-4 times, with 10-30 second collection times. Omnic 8.0 software and Wire 2.0 software was used. The associated microscope is equipped with 10x, 20x, and 50x objectives and a 3 x 4.5 inch stage. Raman was only used to analyze the hand-coloring on the front pastedown in the checkered border around the entire edge of the page. It was not used to further characterize the pigments used for the colored flowers on page 18, due to their location and

pristine condition. While analysis was initially conducted in situ, this technique was not entirely successful, because the paper surface was uneven and challenging to focus on. It was decided that removing samples was necessary. The typical sample size was 1  $\mu\text{m}$  x 20  $\mu\text{m}$ . The close proximity of the hand-colored border to the edge of the page allowed a number of colors from the border to be sampled using destructive techniques without disrupting the appearance of the object. Four colors present in the checkered border, including red, blue, green, and yellow, were analyzed using Raman.

## **2.5 Scanning Electron Microscopy**

Scanning electron microscopy paired with Energy Dispersive Spectroscopy (SEM-EDS) was used to acquire more data related to the elemental composition of the samples, and allowed for mapping of the distribution of elements across the sample surface. Imaging was collected in back scatter electron mode (BSE). A Topcon ABT-60 scanning electron microscope with a Bruker X-flash detector and Quantx model 200 microanalysis was used. Further instrument features include a 22 mm stage height, 20° sample tilt, and 20 keV accelerating voltage. Espirit 1.8 software was used. Three samples were analyzed using this technique, including two samples of the Dutch gilt paper, and one sample from the text block paper. Two samples of the Dutch gilt paper were taken because analysis was first attempted using a cross section of the paper, which was unsuccessful. A second sample of just the face of the paper with applied metal was analyzed. This technique allowed for further characterization of the elements present in both samples on a smaller scale and in greater detail than is possible with XRF.

## **2.6 Fourier Transform Infrared spectroscopy**

Fourier Transform Infrared spectroscopy (FTIR) can collect data related to a wide range of organic materials and some inorganic materials. It was chosen for this project because it can be useful for characterizing adhesives, binders, and some pigments, and is a good complement, or precursor, to gas chromatography-mass spectrometry (GC-MS). A Thermo Scientific Nicolet 6700 FT-IR spectrometer with a Nicolet Continuum FT-IR microscope was used. This instrument conducts approximately 128 scans from 4000 to 650  $\text{cm}^{-1}$  averaged with a spectral resolution of 4  $\text{cm}^{-1}$ . Omnic 8.0 software was used. Three samples were analyzed including two pigment samples, one green and one black, taken from the border of the front pastedown. It was hoped that this technique could help characterize the green and black pigments, since these generally may not

work well with Raman due to the energy levels required to induce vibrations. The third sample was taken from the Dutch gilt paper. However, the main goal was to use this instrument to characterize the binding media used for both the hand-applied colorants and the Dutch gilt paper, since prior characterization of materials allows for more efficient use of GC-MS.

## 2.7 Gas Chromatography-Mass Spectrometry

This analytical technique allows for precise identification of compounds within a set class of materials; for example, it can detect the type and amount of amino acids within a protein sample, or the type and amount of sugars present in a gum. GC-MS served as a complementary technique to FTIR and will allow for further characterization of the binding media present in the Dutch gilt paper, which was suspected to be either a gum or a protein. These adhesives were chosen based on a translated recipe from an early 18<sup>th</sup> century German decorative paper making manual, which indicated that “gum water” was typically used, but also suggested the use of protein based adhesives (Wolfe 2008, 145-149). Two samples of the Dutch gilt paper were analyzed. The goal of identifying the binder material present was to reveal information regarding how the Dutch gilt paper was manufactured. An Agilent 7820A gas chromatograph equipped with an Agilent 5975 mass selective detector (MSD) and an automatic liquid injector was used, along with ChemStation software.

To test the first sample for the presence of amino acids, the sample was first heated for 24 hours with 5.5 M HCl in a vial (100-300 $\mu$ L), and was purged with N<sub>2</sub> during hydrolysis to remove oxygen and water. The samples were then dried. Approximately 50-100  $\mu$ L of a silylating reagent (MTBSTFA and 1% TBDMCS) was added, and the sample was heated again at 60 $^{\circ}$ C for one hour. This exactration process served to remove the amino acids from the sample. The sample was then analyzed. The injector was set to 320 C (splitless mode) with a 9 minute solvent delay. The oven temperature was 55 $^{\circ}$ C for 2 minutes, followed by 325  $^{\circ}$ C at 10  $^{\circ}$ C /min, and then after that a 10 minute isothermal period. The MS transfer line was at 280  $^{\circ}$ C, the source at 230  $^{\circ}$ C, and the MS quad at 150  $^{\circ}$ C.

When testing the sample for gums, the sample was first treated with about 100  $\mu$ L of a 0.5M solution of HCl in methanol at 70  $^{\circ}$ C for 24 hours in a vial (100-300 $\mu$ L). This solution was prepared by adding 400 $\mu$ L of acetyl chloride to 15mL of anhydrous methanol and stirring. The digested samples were dried in a stream of air, and were then treated with a reagent of 3HMDS:9Pyridine:1TMCS (packaged in 1mL glass ampoules). The sample was then heated at

70°C for one hour, and was again dried using an air stream. Approximately 100µL of hexane was then stirred with the residue, and this extracted only the non-polar silylated material into solution. The solution was then placed into vials and injected. The injector was set to 320 C (splitless mode) with a 9 minute solvent delay. The oven temperature was 55°C for 2 minutes, followed by 325 °C at 10 °C /min, and then after that a 10 minute isothermal period. The MS transfer line was at 280 °C, the source at 230 °C, and the MS quad at 150 °C.

### 3. RESULTS

#### 3.1 Fiber Identification

The fiber contents of all four samples are described below in Table 2. Samples were compared to known references, and were evaluated based on the presence of lumen, the presence of nodes, and birefringence. The text block paper, cover paper, and sewing thread were all found to contain bast fibers, likely linen. The formerly blue ribbon was found to contain silk fibers. While the fibers from the text block were examined for the presence of smalt, for reasons that will be discussed later, results were inconclusive. Small particles of a uniform color, uniform size, and amorphous shape were present, but were too small to be positively identified as pigment at the available magnification.

**Table 2: Fiber composition of sewing materials and papers**

Sample location	Fiber Composition	Other contents
Sewing thread	Bast fiber, likely linen	-
Sewing ribbon	Silk <sup>6</sup>	-
Cover paper	Bast fiber, likely linen	Possible pigment or dirt particles
Text block paper	Bast fiber, likely linen	Possible pigment or dirt particles

#### 3.2 Examination using Ultraviolet Radiation

No fluorescence due to exposure to ultraviolet wavelengths was detected. However, many of the oily looking stains, which occur on pages throughout the text block, appeared a deep black, as did the Dutch gilt paper on the cover. This indicates that a water event caused some of the metal-containing pigment from the Dutch gilt paper cover migrated onto the manuscript pages.

<sup>6</sup> It should be noted that, upon contact with tweezers for sampling, the thread quickly disintegrated, which is often a characteristic of aged silk.

### 3.3 X-Ray Fluorescence Spectroscopy

XRF data was collected from numerous locations including the hand-colored flowers, the hand-colored colophon, the Dutch gilt paper, and the iron gall type ink. Please note that the elements found in all measurements of the background reading of the paper are consistent across all three measurements, and include the elements arsenic and iron. It is also important to note that the attempts to analyze the colophon resulted in finding the same elements which were found in analysis of the Dutch gilt paper. Also, three visually different reds were analyzed, and all three were found to contain different elements. The blue pigment contained only high amounts of iron, while the green pigment contained high amounts of lead and iron. The elements detected and their corresponding locations are shown below in Table 3.

**Table 3: XRF Samples and Elements Detected**

Sample name (Page )	Measurement location	Observed color	Elements detected
Paper substrate 1 (18)	1 Lower right quadrant	Text block paper	<b>As, Fe, Co, Ni, Cu, K, Ca, S</b> <sup>7</sup>
Paper substrate 2 (18)	2 Lower center border	Text block paper	<b>As, Fe, Co, Ni, Cu, K, Ca, S</b>
Paper substrate 3 (10)	3 Lower right quadrant	Text block paper	<b>As, Fe, Co, Ni, Cu, K, Ca, S</b>
Green leaf (red flower) (18)	4 Lower right quadrant	Green	<b>Pb, Ca, Fe</b> <sup>8</sup>
Red flower (18)	5 Lower right quadrant	Red-pink	<b>Hg, Ca, K, S</b>
Blue flower (18)	6 Upper right quadrant	Blue	<b>Fe</b>
Orange flower (18)	7 Upper right quadrant	Orange	<b>Pb, Ca, Mn</b>
Yellow letter (18)	8 Upper left quadrant	Yellow	<b>None</b>
Dark red flower (18)	9 Upper left quadrant	Deep red	<b>Fe, Ca, S</b>
Colophon	Lower right quadrant	Yellow	<b>Cu, Zn</b>
Back Cover <sup>9</sup>	Lower left corner	Bronze	<b>Cu, Zn</b>
Front Cover <sup>3</sup>	Lower left corner	Bronze	<b>Cu, Zn</b>
Ink on Letter <sup>3</sup>	Letters L, F, and I	Black-brown	<b>Fe, K</b>

<sup>7</sup> Bold font indicates major elements. Rh is present in all spectra.

<sup>8</sup> Assume that elements found in the paper substrate are present in all of the remaining spectra collected, in identical quantities, unless otherwise noted.

<sup>9</sup> Three measurements each were taken for the back cover, the front cover, and the iron-gall ink (9 measurements total), to assure the materials present were consistent. See Appendix A for descriptions of the sample locations.

### 3.4 Raman Spectroscopy

Further analysis of the colorants on the front pastedown was conducted to confirm the XRF findings. XRF could not be used successfully on the pastedown, because the Dutch gilt paper on the other side overwhelmed any data related to the pigments, so analysis using Raman and FTIR was conducted. The red, yellow, blue, and green pigments in the pastedown border were identified, and the results are listed in the Table 4 below. *Please refer to Appendix D for the Raman spectra.* The spectrum the red sample had the least amount of interference, and was a clear match for the vermilion reference. For the yellow sample, the only identifiable peak occurred at 1592 consistently, and this was therefore the only peak which matched the reference for gamboge. The blue sample had all of the same peaks as the reference for Prussian blue, although the major and minor peaks differed slightly. The spectra for the green sample are included below, because ultramarine was detected in this sample, and this was unexpected. Only one peak for lazurite, at 822, was shown in the reference, but was not detected in the sample. Gamboge was also detected in this sample, based on the same peak as was found in the yellow sample.

**Table 4: Raman Spectroscopy Results**

Color of sample	Pigment identified	Peaks measured <sup>10</sup>	Reference peaks
Red	Vermilion	<b>253, 285, 344</b>	<b>252, 282, 343</b>
Yellow	Gamboge	<b>1592</b>	1215, 1246, 1265, 1330, 1433, <b>1592</b> , 1633
Blue	Prussian blue	<b>282, 538, 2102, 2154</b>	282, 538, 2102, <b>2154</b>
Green	Gamboge	<b>1591</b>	1215, 1246, 1265, 1330, <b>1433, 1592, 1633</b>
	and Lazurite (Ultramarine)	<b>260, 548, 1095</b>	258, 548, 822, <b>1096</b>

<sup>10</sup> Bold indicates major peaks, for both the sample column and reference column in this table.

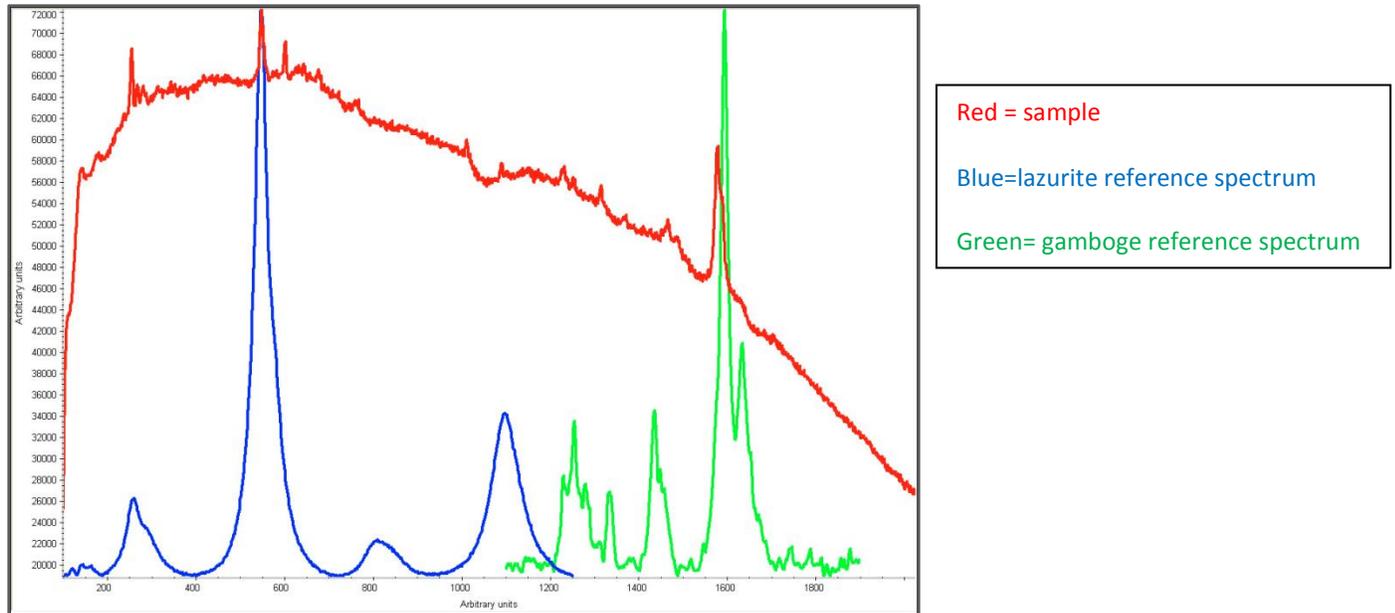


Fig. 8: Raman spectrum for the green sample from the pastedown

### 3.5 Scanning Electron Microscopy (SEM)

SEM-EDS indicated that small silicon particles with trace amounts of associated arsenic were detected within the sample from the text block paper, although no cobalt could be detected using this analytical technique.

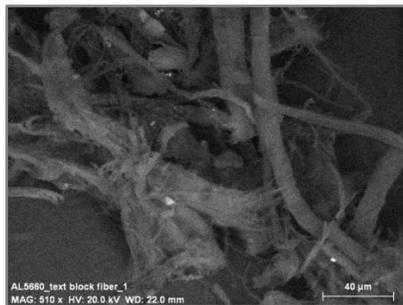


Fig. 9: BSE image



Fig.10: EDS, Silicon

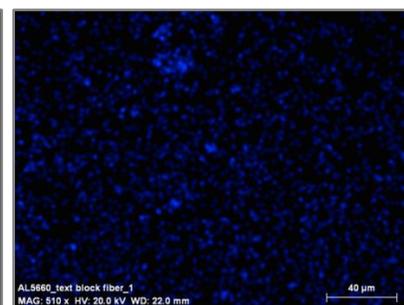


Fig. 11: EDS, Arsenic

SEM-EDS also indicated that copper and trace amounts of zinc were present in the Dutch gilt paper sample, and this too confirmed the preliminary XRF result. In addition, SEM-EDS revealed the high amounts of chlorine associated with the copper throughout the sample.

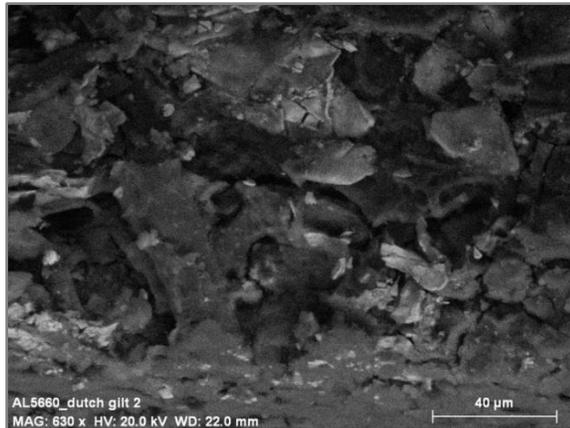


Fig. 12: BSE image of Dutch gilt sample

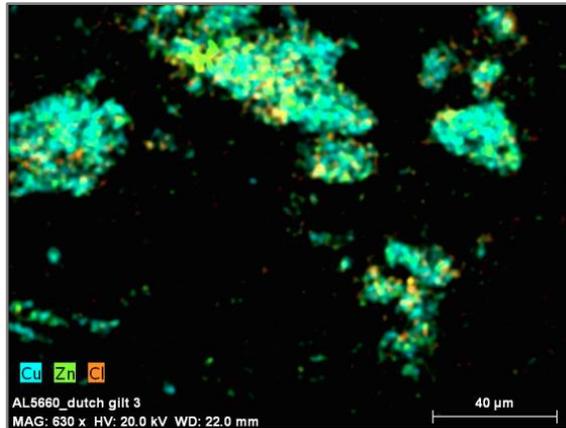


Fig. 13: EDS, with Cu, Zn, and Cl

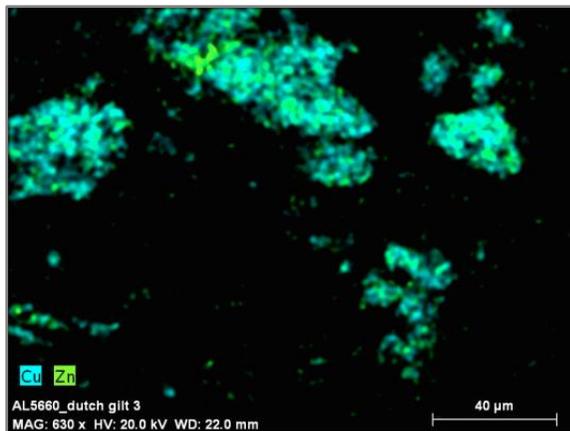


Fig. 14: EDS with Cu, Zn

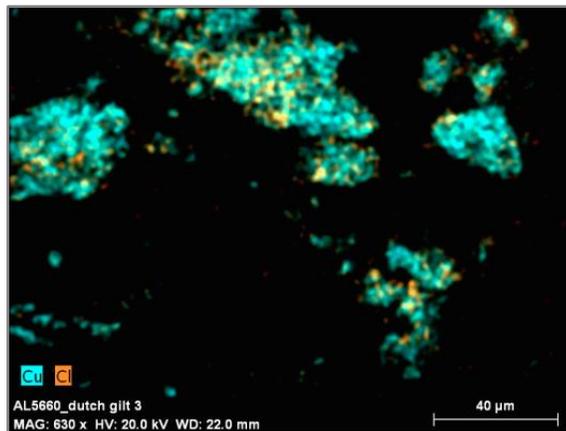


Fig. 15: EDS with Cu, Cl

### 3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Of the three samples analyzed using FTIR, only the spectra from the green sample provided useful data; the spectra for both the black sample and Dutch gilt paper sample only matched the reference for cellulose, which indicated that only the paper supports were detected. It is likely that any binding medium present in these samples was below the detection limits of the instrument. Analysis of the green revealed provided a spectrum with peaks that strongly corresponded to references for gum Arabic, chalk, and gypsum. The spectrum for the green sample and the corresponding references are shown in the figure below. The numbers above indicate matching peaks, which are indicated by the blue bars.

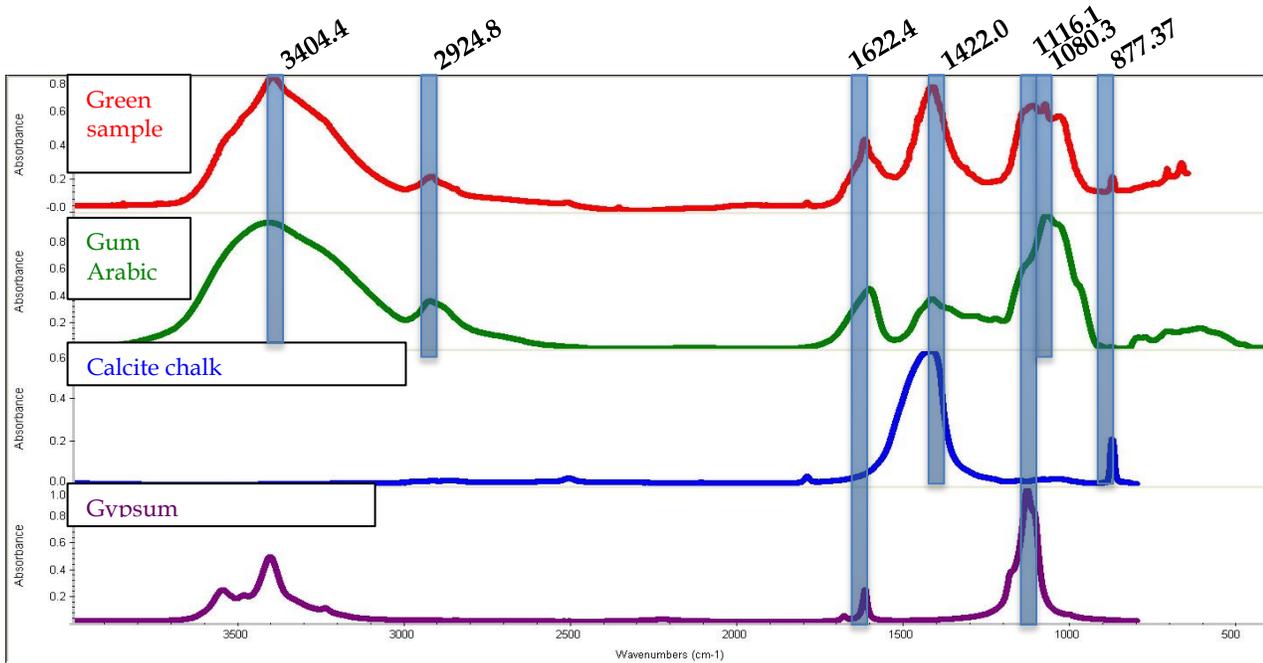


Fig. 16: FTIR results for the green sample from the pastedown

### 3.6 Gas Chromatography-Mass Spectrometry (GC-MS)

Analysis indicated that no gums were present, but a small amount of protein is present. Five amino acids were detected, including alanine, glycine, valine, leucine, and glutamic acid. *Please refer to Appendix E for the spectrum for the amino acids.*

## 4. DISCUSSION

### 4.1 Fiber Identification

The fiber contents of the materials examined, including the sewing materials and paper, were not surprising. Linen was historically used for sewing books, and continues to be the sewing material of choice among bookbinders today. The use of linen for the repair sewing was therefore anticipated and is not uncommon. It was also suspected that the ribbon was silk, due to its overall appearance and state of deterioration. This material is also appropriate for the object's historic time period, although it would have been unusual for a ciphering book.

## 4.2 Examination using Ultraviolet Radiation

The deep black stains observed throughout the text block suggest that some previous water event may have caused the metal particles present in the Dutch gilt paper to migrate into numerous regions of the text block. The overall lack of fluorescence suggests that no fluorescent ink, pigment, or adhesive is present.

## 4.3 X-Ray Fluorescence Spectroscopy

Some of the elements found in the paper support, especially cobalt and arsenic, are usually associated with smalt (Harley 1970, 51-53; Gettens and Stout 1966, 157; Roy 1993, 113-130). This was surprising, because the paper does not appear blue. However, numerous sources mention that smalt was, at this time, added to paper during production as “blueing”; it would have functioned like optical brighteners, in that yellow fibers would appear bluer, and therefore brighter white, in the viewers’ eyes (Krill 2002, Perkinson 1997, Brückle 1993).

The pigments found on the pages which could be analyzed using XRF were not surprising overall, and are contemporary with the time period and geographical location of the object. Overall, any calcium, potassium, and magnesium are considered impurities in the paper or pigment. The analysis of the colorant used for the green leaf was largely inconclusive. A relatively strong presence of lead was detected, and as there are no known lead-containing green or blue pigments, it must be concluded that the green color consists of a lead containing yellow and a relatively undetectable blue. It is somewhat possible that Prussian blue may be responsible for the slight increase in Fe. The exact yellow present remains ambiguous; while chrome yellow would be appropriate for this time period, no chromium was detected (Making Fancy 2005). The sample analyzed on the yellow letter showed no change in detected elements in comparison to the spectra for the paper substrate, which suggests an organic yellow colorant may be present. This would also be appropriate for the late 1700s, and has been identified on numerous fraktur objects at Winterthur (Winterthur 2004).

**Table 4: Pigments found on page 18 using XRF analysis**

Sample name	Location	Observed color	Elements detected <sup>11</sup>	Probable pigments
Green leaf	4	Green	Pb, Ca, Fe	Lead-containing yellow , Prussian blue
Red flower	5	Red-pink	Hg, Ca, K, S	Vermillion <sup>12</sup>
Blue flower	6	Blue	Fe	Prussian blue <sup>13</sup>
Orange flower	7	Orange	Pb, Ca, Mn	Red lead <sup>14</sup>
Yellow letter	8	Yellow	None	Organic yellow
Dark red flower	9	Deep red	Fe, Ca,S	Red oxide <sup>15</sup>



Fig. 17: Page 18 XRF sample locations

<sup>11</sup> Only the major elements detected are indicated in this chart, because only the major elements were considered when determining which pigments were most likely present.

<sup>12</sup> Gettens and Stout 1966, 170-172; Harley 1970, 114-117; Roy 1993, 159-182

<sup>13</sup> Gettens and Stout 1966, 149-151; Fitzhugh 1997, 191-217

<sup>14</sup> Gettens and Stout 1966, 152-154; Feller 1986, 109-140

<sup>15</sup> Gettens and Stout 1966, 122; Berrie 2007, 39-109

The inability to analyze the pigments present on the pastedowns using XRF was unanticipated. While XRF has the reputation of being a surface analysis technique, the depth of penetration was clearly too great for analysis of the pastedowns, and resulted in too much interference from the Dutch gilt cover materials. Because of the presence of the Dutch gilt paper, Raman spectroscopy is a more appropriate option for analyzing the pigments used on the pastedowns.

The high iron content of the ink shows that it is in fact iron gall ink, which was suspected based on its visual appearance and state of degradation. Since it was found on three pages in different locations throughout the book, it may be assumed that iron gall ink was used throughout the manuscript. This is also an appropriate and expected material which was common in the late 18<sup>th</sup> century. While the strong presence of copper on the Dutch gilt cover is generally indicative of bronze, the presence of tin would be expected instead of zinc, which usually indicates brass. A variety of metals, including bronze and silver, were used historically to create Dutch gilt paper (Wolfe 2008). The use of SEM assisted in clarifying these results, and will be discussed later.

#### **4.4 Raman Spectroscopy**

Almost all of the pigments found were commonly available to artists in America at the time, including vermilion, gamboge, and Prussian blue. It was not surprising that the red was vermilion, since it is used on page 18. It was also confirmed that the blue is Prussian blue, and that the yellow in the border is gamboge. While it was expected that green would be a mixture, it was assumed that a mixture of gamboge and Prussian blue would have been used. While the green areas do contain gamboge, ultramarine was present. This was unexpected, because this pigment would have been prohibitively expensive, even for the Barrell Family, and usually would not have been mixed with yellow to make green. For the green sample analyzed using XRF, this sample may also contain ultramarine, which would explain the ambiguous results.

#### **4.5 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)**

The SEM results regarding the smalt within the text block paper helped to confirm the initial XRF findings, and also expand on John Krill's findings in his book, *English Artist's Papers* (2002, 139-145). The color-mapping of distribution of elements within the sample showed that the trace amounts of arsenic were associated with the silicon, which indicates that the particles are most likely smalt. The shape of the particles was difficult to see, so it could not be confirmed if

they were glassy. When using XRF, high amounts of arsenic and small amounts of cobalt were detected, but cobalt was not detected using SEM. This was likely because cobalt is present in trace amounts which were below the detection limits of this instrument. Cobalt has high covering power, so a relatively small amount of smalt would need to be present in order to alter the appearance of the paper only slightly.

The chlorine associated with the copper in the Dutch gilt paper sample indicates the widespread presence of more corrosion products than was anticipated. The corrosion does not appear to correspond to areas which were damaged by the water event. The corrosion also helped to confirm one detail regarding the manufacture of the Dutch gilt paper. One recipe which was consulted states that, ““These papers are either monochrome or covered with a pattern. For the simple ones you **employ counterfeit milled gold [pulverized bronze]**; and counterfeit milled silver, **which is ground down with gum water and then, as is customary, thrown on with an artist’s brush** (Wolfe 2008, 145).” It seems likely that a “pulverized” metal may have been used to create the Dutch gilt paper on this object. The appearance of the surface differs significantly from that of metal leaf applied to paper, and the presence of many small metal particles would also explain the universal presence of corrosion products. There would be a greater amount of surface area exposed, and the metal would degrade faster than if it were in sheet form.

#### **4.6 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR revealed that gum arabic was used as the binding medium for the pigments. We also found evidence of chalk and gypsum, which likely indicates the presence of some filler material. FTIR was likely unsuccessful for analyzing the binding medium of the Dutch gilt paper because any adhesive is highly degraded and is only present in trace amounts. Also, it was not possible to isolate the adhesive from the paper support, and this also deterred detection of any adhesive.

#### **4.7 Gas Chromatography- Mass Spectroscopy (GC-MS)**

It is surprising that gums were not detected, since “gum water” is suggested in the recipe which was consulted (Wolfe 2008, 145-149). Another recipe within the same book mentions the use of isinglass and animal glue, but only for attaching silver to paper, and the author suggests these are not commonly used (Wolfe 2008). Based on the presences of numerous amino acids, it seems likely that a dilute, animal-based adhesive may have been used. Hydroxyproline was not detected therefore the presence of animal glue cannot be confirmed with confidence.

## 5. CONCLUSION

Overall, some materials that were found were expected, including gum arabic as the binding medium and pigments that were used by artists in America during this time period. There were also some surprises, including ultramarine mixed with gamboge, and smalt within the text block paper. However, when the social and economic status of the Barrell Family is considered, Charles' use of unusually expensive materials is not entirely surprising. Like many upper-class 13 year olds in Boston, Charles was probably hoping to go to college at age 14, and it seems likely that he prepared this book as a portfolio of his best work. Charles probably wanted to use the best materials he had, and just happened to have the most expensive materials at his disposal. The fact that Charles was learning geometry may suggest that he was unusually well-educated, or perhaps that he planned to enter a navigation-related profession.

Acquiring a greater understanding of the materials present did not have a large impact on the treatment of this object. Because this book is in fairly good condition, little treatment was needed besides minimal surface cleaning, re-sewing the text block, and stabilizing the original sewing materials. However, the condition of the Dutch gilt paper is now of more concern, because of the amount of corrosion present. A stable environment is now even more important for this book.

As no other technical study of a ciphering book has been conducted, and no large survey of the materials used to create these object has been conducted, there is definitely room for more research into the material composition of these manuscripts. Charles' book proved to be an unusual book to start with, because it is not representative of what the average student might have created. As was mentioned earlier, there are 10 other math exercise books within the Downs Collection which include hand-applied colorants, and any of these would make excellent candidates for analysis. In the future, it would also be to useful to look more closely at the materials college students used to create exercise books, in order to gain a greater understanding of how older students' work might compare.

## 6. ACKNOWLEDGEMENTS

Dr. Caitlin O'Grady and Catherine Matsen assisted in supervising the use of analytical equipment for this study, and provided suggestions for writing and organizing this report. Laura Parrish, Associate Librarian, of the Downs Collection, provided assistance with the survey of the ciphering books. Book conservator Chela Metzger is overseeing treatment of this book, and has suggested many helpful resources. Paper conservator Joan Irving provided helpful insight and resources related to researching the use of pigments on paper in colonial America. The reports of a number of former and current WUDPAC students were also referred to as guides for organizing this report.

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XRF Analysis of hand coloring. Unpublished database. Printed 11/16/2004. Courtesy of Joan Irving. Winterthur Museum and Library, Winterthur, DE.

Appendix A  
Images of watermarks from text block paper

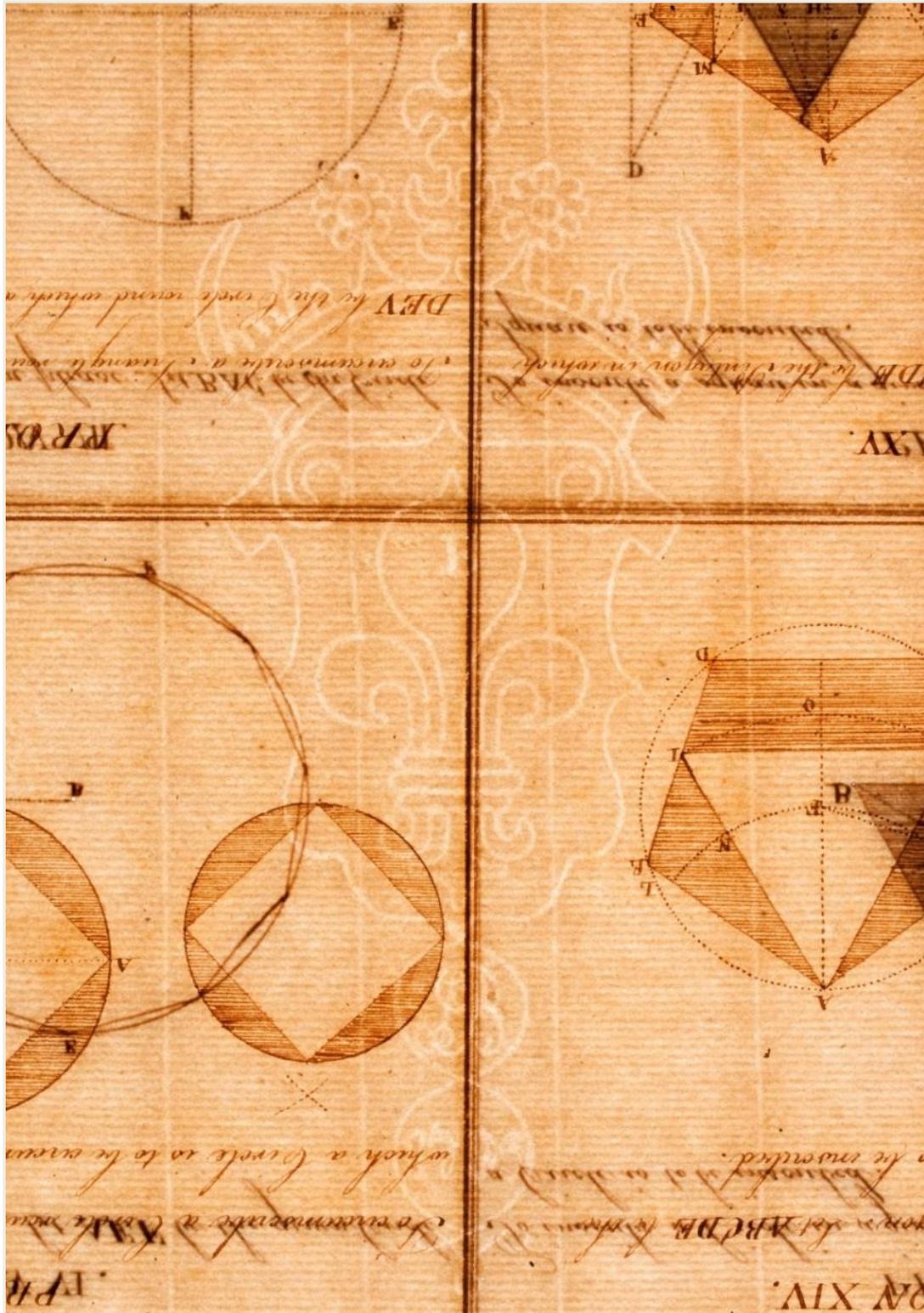


Fig. 18: Watermark

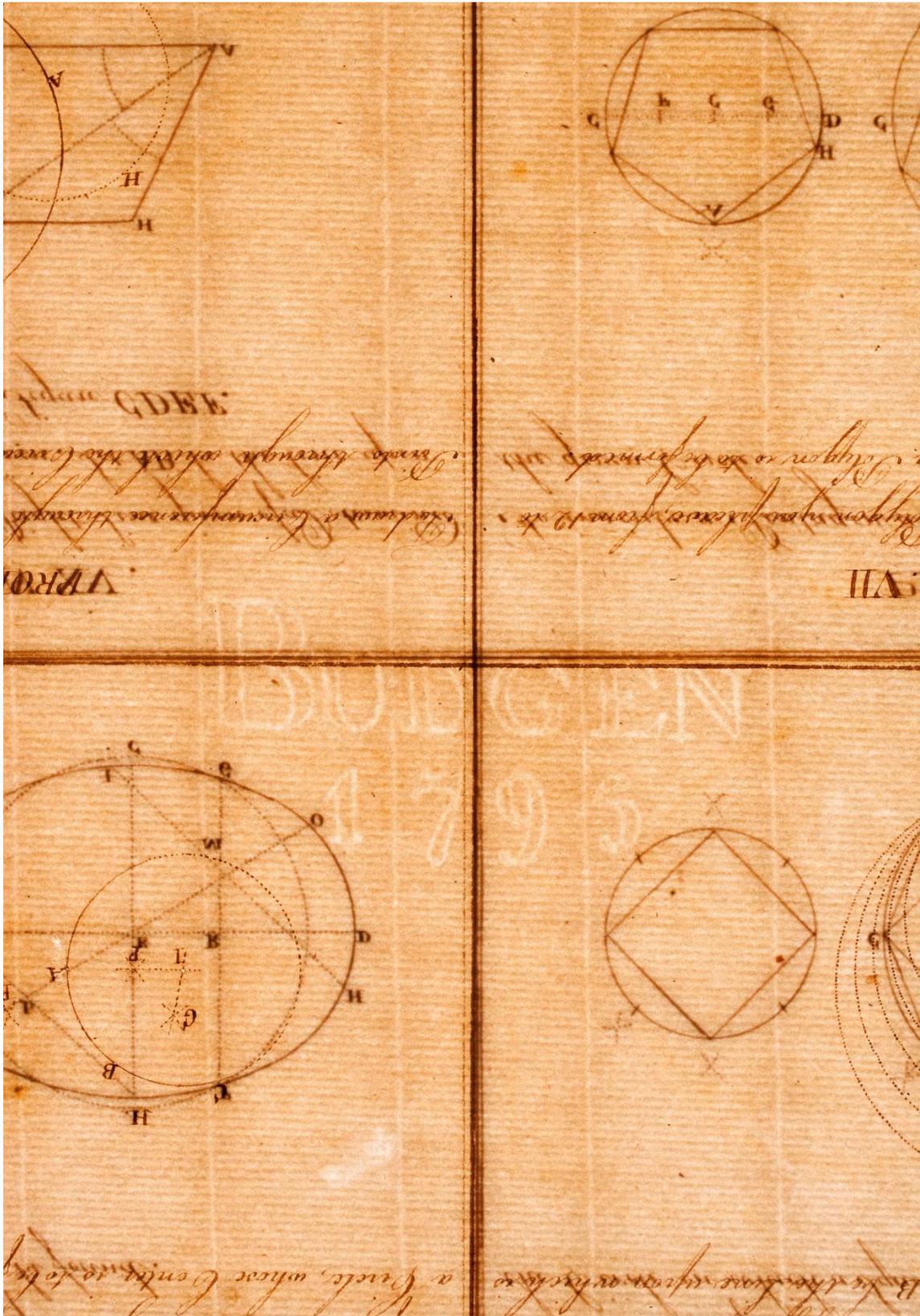


Fig. 19: Countermark

## Appendix B

## Summary of Survey of Mathematics Exercise Books in Winterthur's Downs Collection

Call number	Author/creator	Date	Height (cm)	Number of sections	Cover materials	Color
Doc. 735	Earl, Thomas	~1727	34	Multiple	Leather, scabbards	Yes
Doc. 784	Calwell, Thomas	~1750	31	Single	Paper (ream wrapper)	No
Doc. 743	Bawden, Isaac	1763-5?	25	Multiple	Leather, mill boards	No
Doc. 887	Eastabrook, Calvin	1764-6	33	Single	Unknown	Red
Doc. 1238	Bordman, W.	1774	32	Single	Coarse brown paper cover, marbled paper flyleaf	Yes
Doc. 1442	Clayton, Peggey	1776	33	Single	Burlap-like textile, Newspaper	Yes
Doc. 463	Shields, James	1787-8	21	Multiple	Leather (tooled suede)	Yes
Doc. 782	Myers, Jacob	1789	34	Single	Unknown	Yes
Doc. 783	Tomlinson, Charles	1790-1810	34	Two	Leather spine, paper boards	No
Doc. 607	Beach, Laura	1791-1808	22	Multiple	Paper cover	No
Doc. 1239	Rider, Weeden	1795-1803	34	Three	Paper cover	No
Doc. 153	Bush, Samuel	1795-1823	36	Unknown	Leather with paper sides	No
Doc. 1067	Miller, Godfrey	1800	33	Single	Decorative paper cover	No
Doc. 863	Parker, M.S.	~1800-9	31	Single	Blue paper, printed	No
Doc. 1068	Lewis, Thomas	1801	34	Single	Marbled paper cover	No
Doc. 793	Prentiss, Caleb	1803	34	Two	Decorative paper cover, coarse paper for pastedown	No
Doc. 868	Hewlett, Oliver	1803-5	35	Two	Decorative paper and coarse brown paper	No
Doc. 425	Eckman, John	1804	31	Multiple	New cover (recent conservation work)	Yes
Doc. 615	Merrick, Thomas T.	1810	34	Multiple	Quarter bound with blue paper sides and leather spin, pulp boards	Yes
Doc. 1518	Moore, William	1811	24	Multiple	Half bound with leather and marbled newsprint sides, mill board	No
Fol. 379	Waltrous, Jabez	1813	35	Single	Wallpaper cover, manuscript written in blue ink	Only blue ink
Doc. 1254	Morrison, Hamilton	1816-17	32	Single	Roughly tanned leather, lined with newsprint	No
Doc. 377	Boody, P.	1818	32	Multiple	Vellum laced case binding	Minimal
Fol. 82	Bass, F.W.	1819	51	Three	Burlap-like textile cover, iron gall ink in bad condition	Minimal
Doc. 414	Heald, Jacob	1819-29	26	Multiple	Leather with marbled paper sides, boards	No
Doc. 791	Potter, Robert M.	1820	33	Single	Decorative paper cover	No
Doc. 847	Rowley, Samuel	1820-29	30	Single	Blue paper (printed)	No

## APPENDIX C

Sample locations (Arranged in chronological order of when sampling occurred)

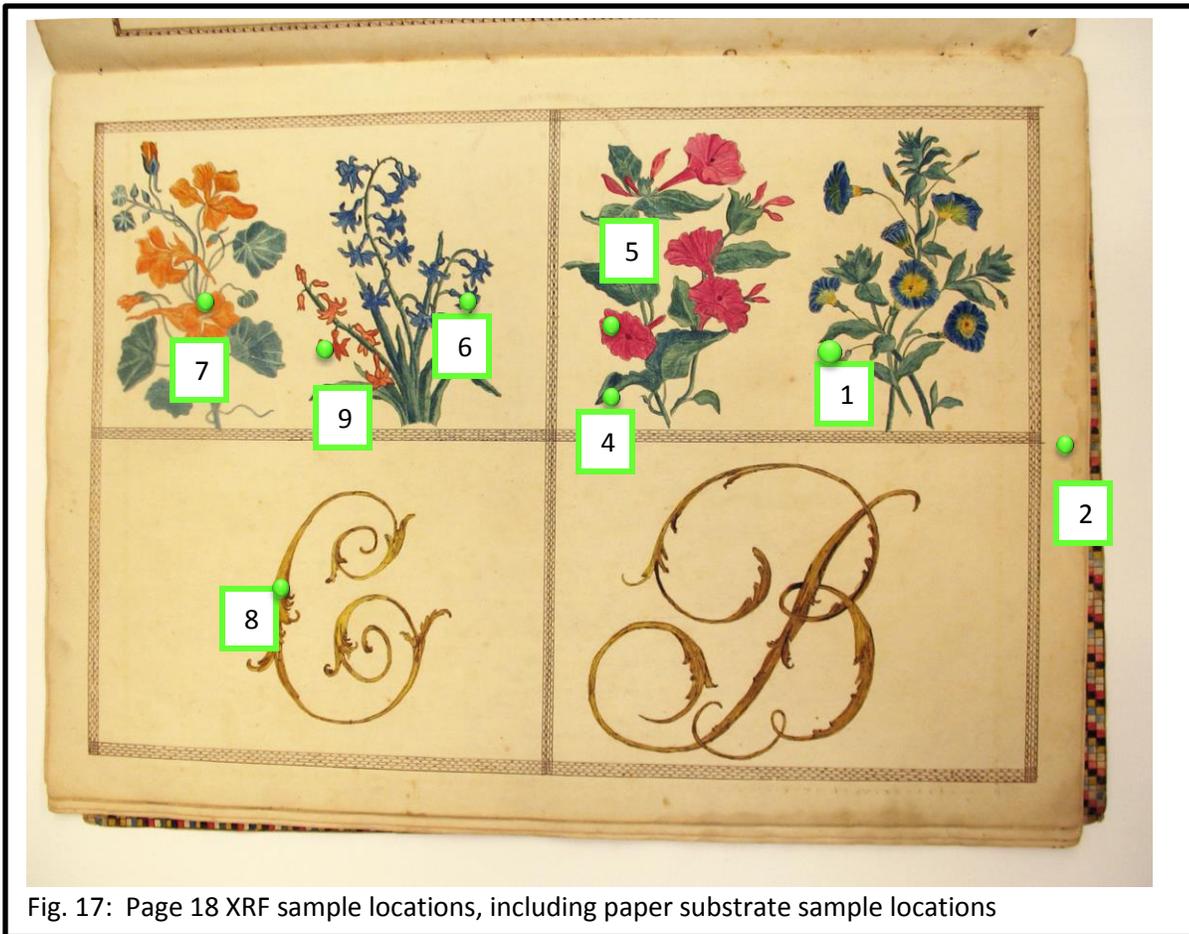


Fig. 17: Page 18 XRF sample locations, including paper substrate sample locations

**Table 5: Page 18 Sample Locations**

Sample Number	Sample Name
1	Paper substrate 1
2	Paper substrate 2
4	Green leaf (red flower)
5	Red flower
6	Blue flower
7	Orange flower
8	Yellow letter
9	Dark red flower

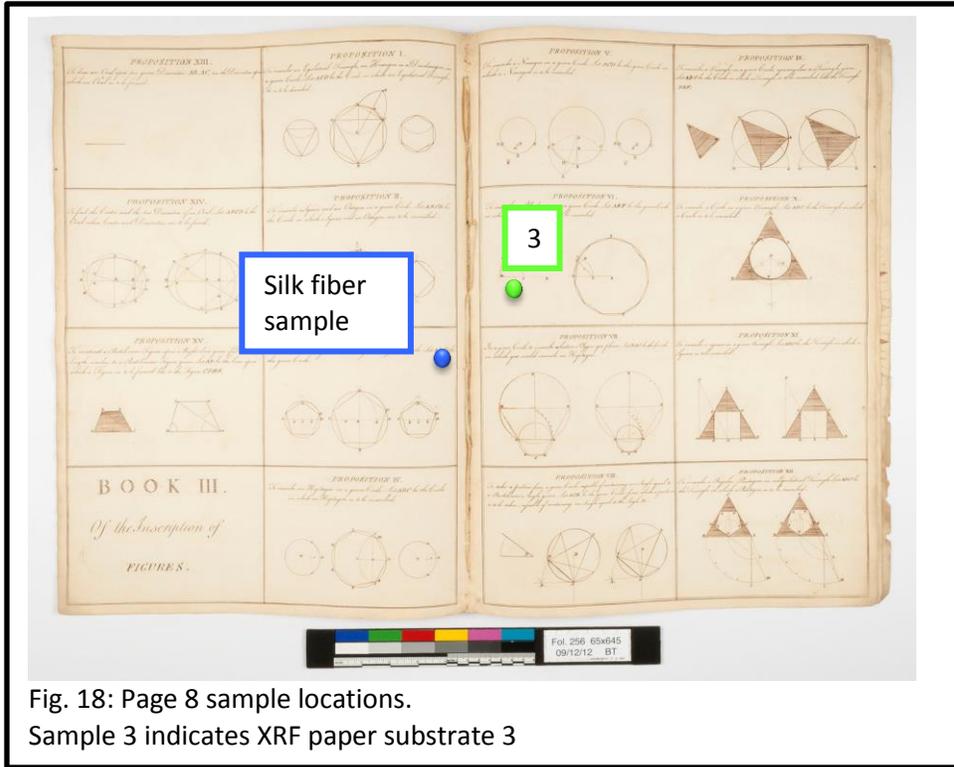


Fig. 18: Page 8 sample locations.  
Sample 3 indicates XRF paper substrate 3



Fig. 19: Back pastedown, Sample 10 Colophon Yellow  
(inconclusive XRF sample)

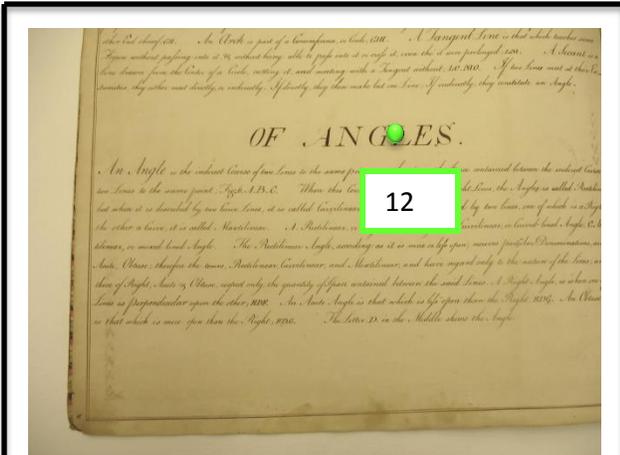


Fig. 20: XRF Letter L Ink sample location p.2



Fig. 21: XRF Letter F Ink sample location p. 8

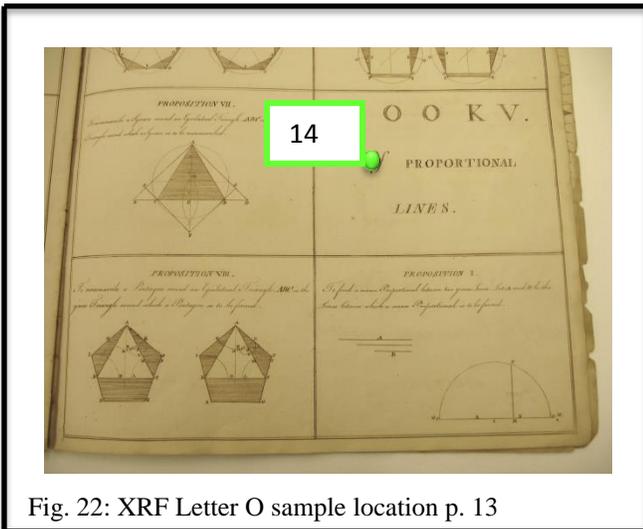
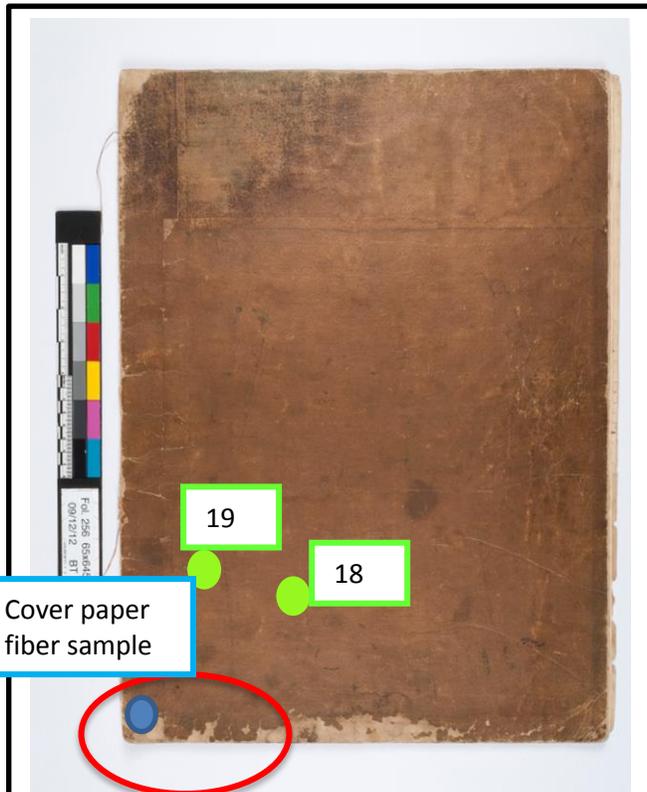


Fig. 22: XRF Letter O sample location p. 13



Cover paper fiber sample

Fig. 11: Front cover XRF Samples in green, paper fiber sample in blue. Red indicates sampling area for SEM, FTIR, and GC-MS

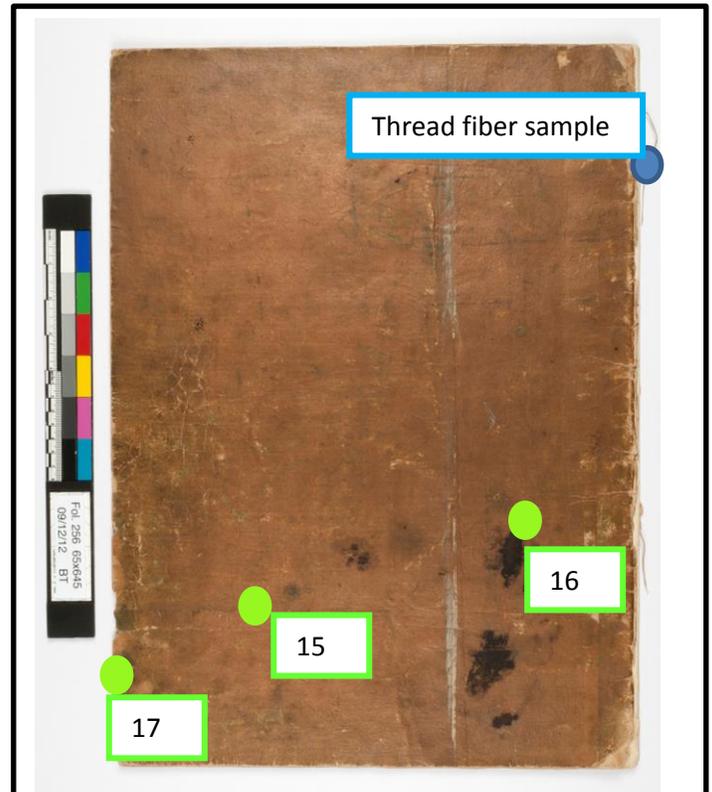
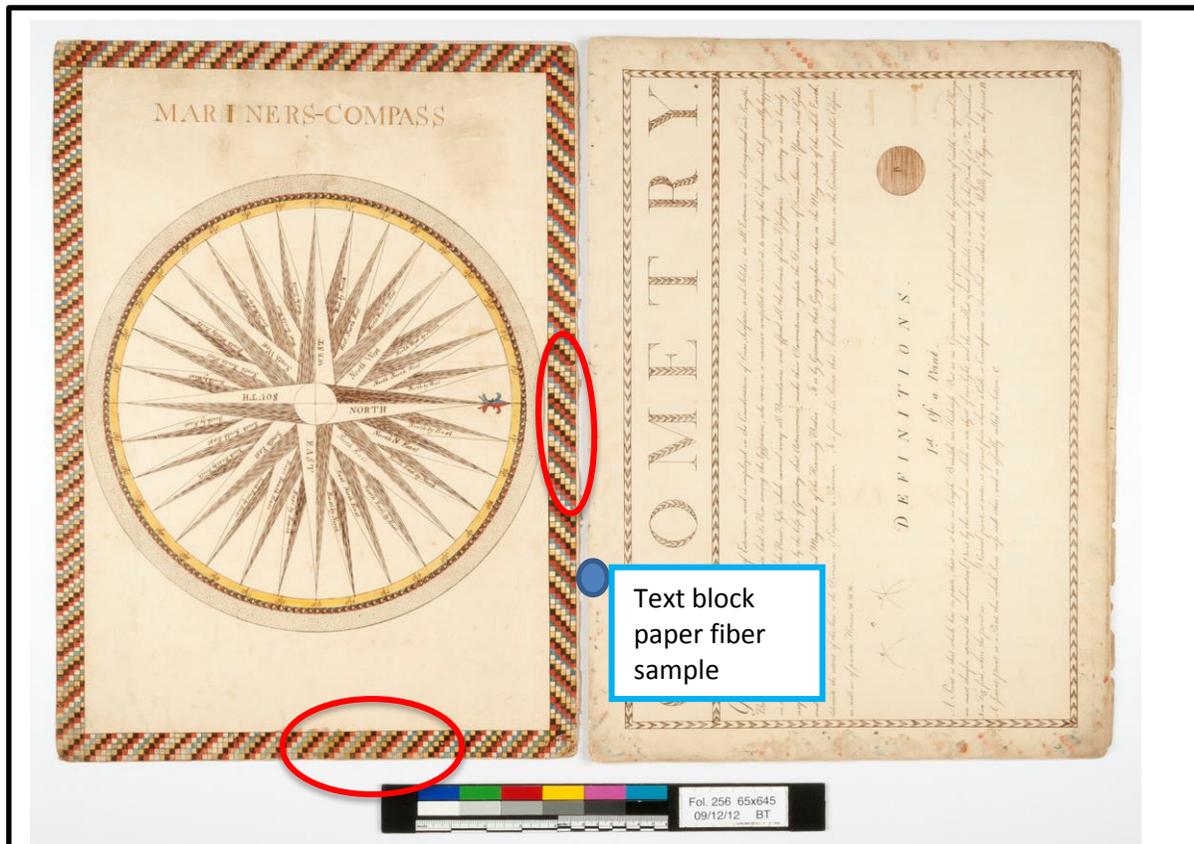


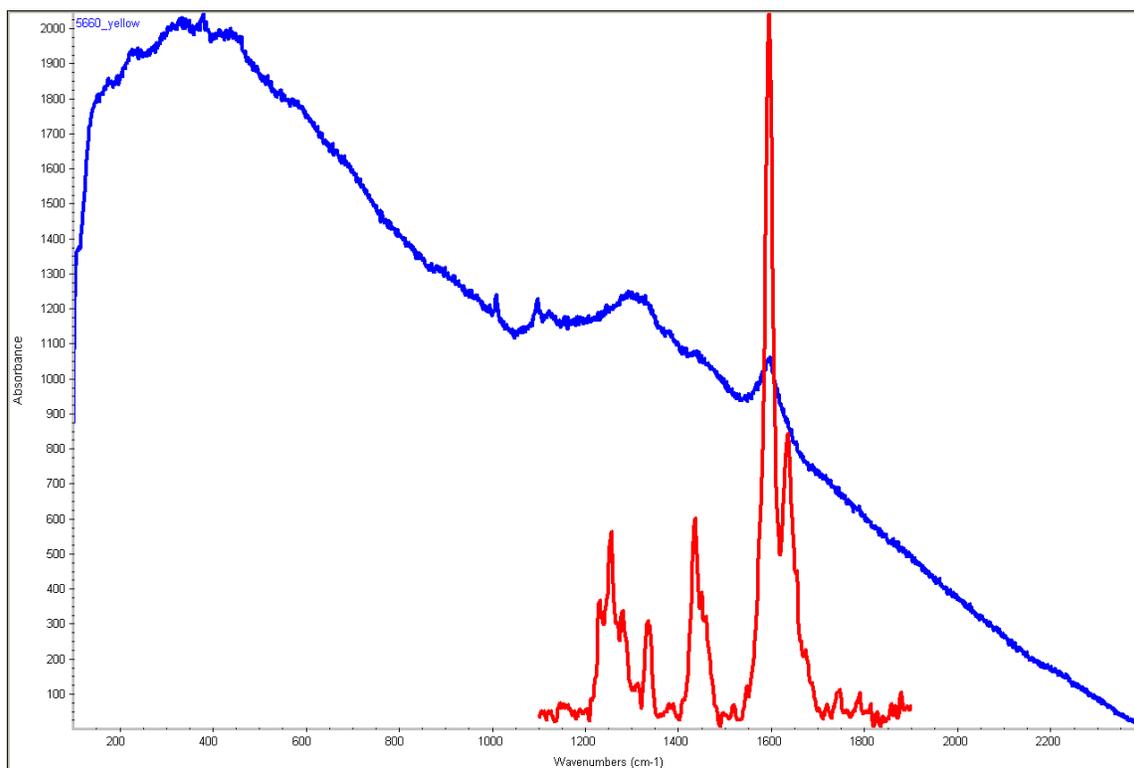
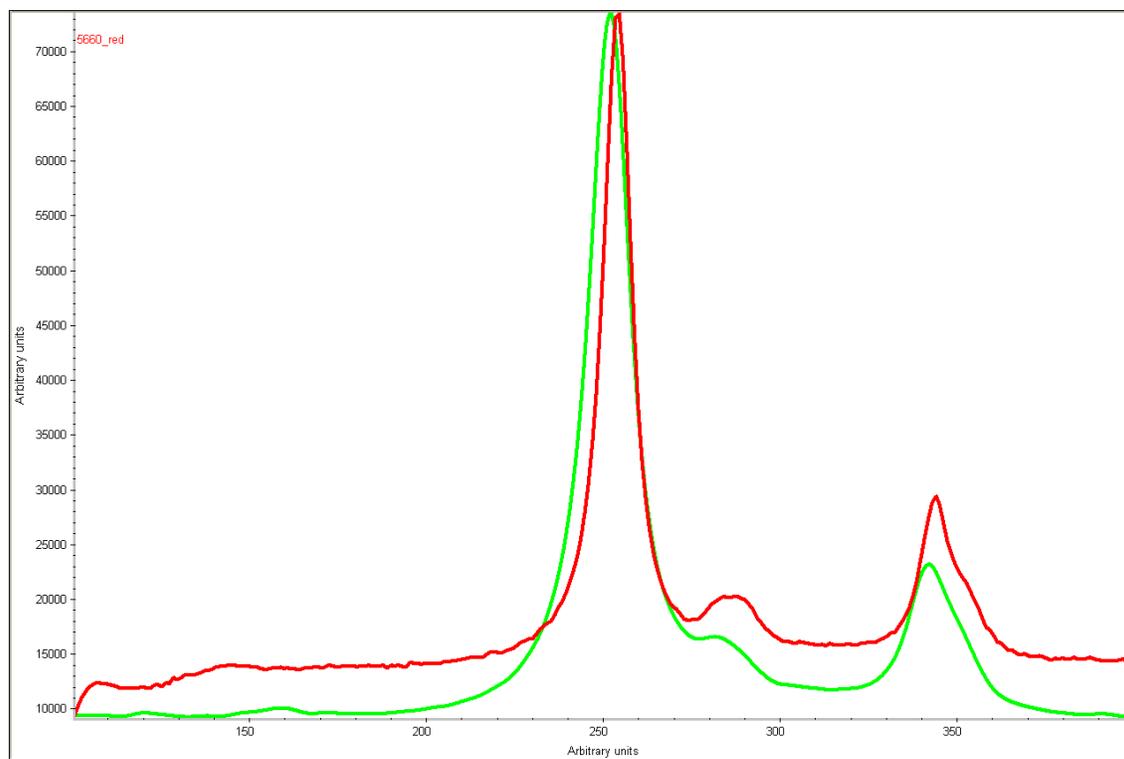
Fig. 12: Back Cover XRF Samples, Thread sample

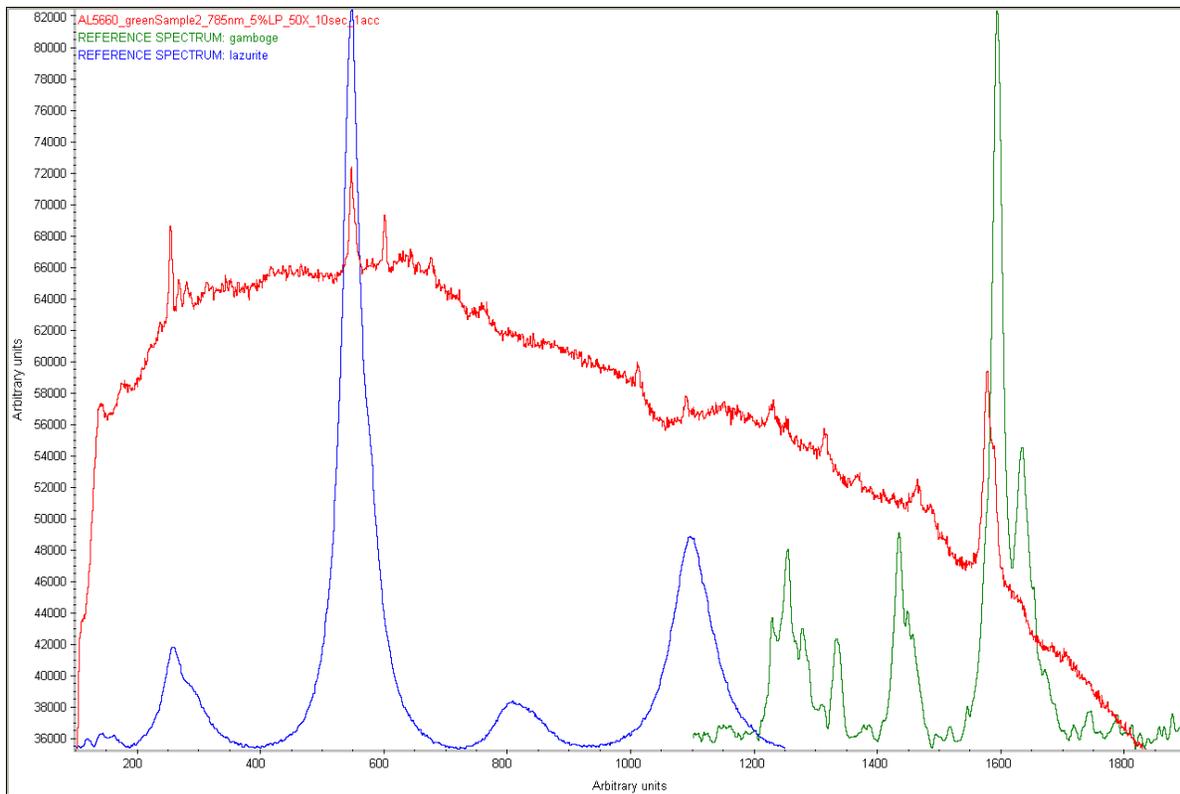
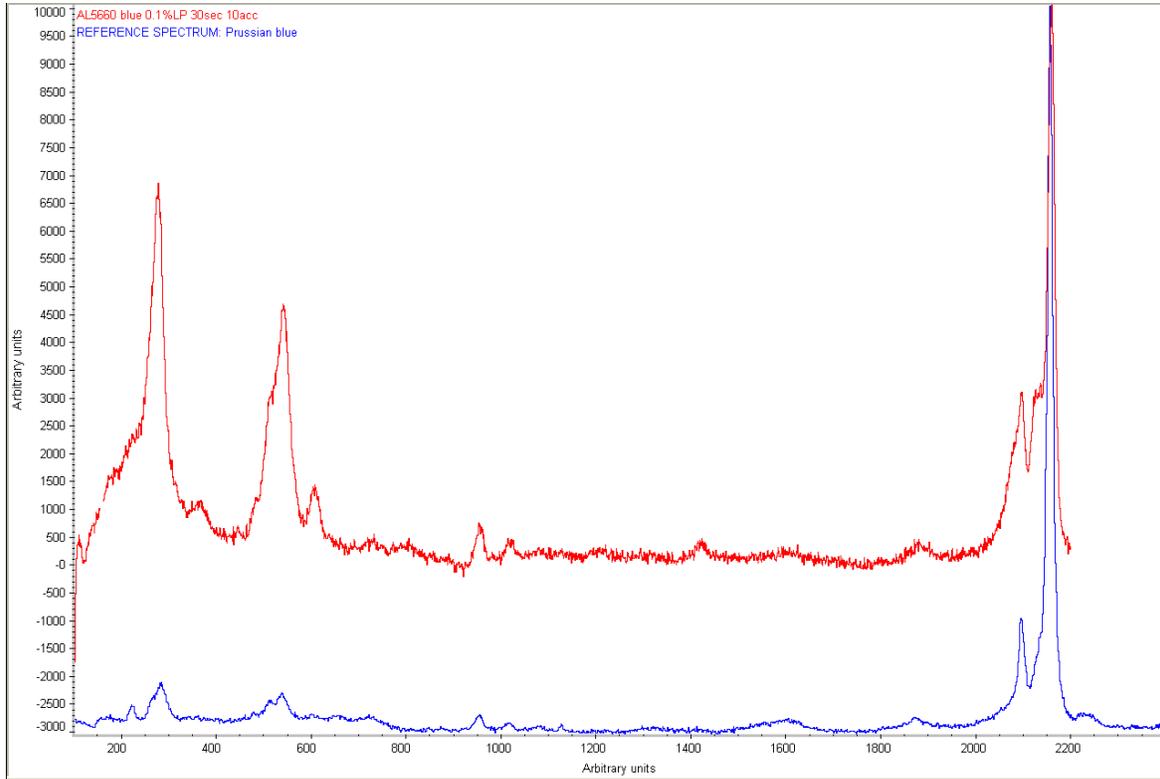


Text block paper fiber sample

Fig. 10: Front pastedown and first page. Blue indicates paper fiber sample location. Red circle indicates suitable sampling area for Raman, SEM, FTIR, and GC-MS samples.

## Appendix D Raman Spectra





## Appendix E GC-MS Spectrum

