Investigating the Juniata College Collection of Pennsylvania German Fraktur: Art Historical Perspectives and Scientific Analysis Richard R. Hark, Katelyn R. Houston, Jennifer Mass, Lisa Minardi, Hedwig T. Durnbaugh, and John Mumford

Bookend Seminar given by Richard Hark, March 21, 2012

Richard R. Hark is Professor of Chemistry at Juniata College.

Juniata College has an impressive collection of over 50,000 manuscripts and rare books in its Special Collections, including many items of importance to colonial American history and especially the rise of Anabaptism in Europe and America. It is considered one of the top German-American research repositories in the United States.¹ Most of the collection comes from the library of Abraham Harley Cassel, a nineteenth-century bibliophile who assembled one of the largest collections of German-American rare books and items in the world.² The Juniata holdings include illuminated manuscripts, material from Ephrata Cloister and Snow Hill Nunnery, hymnals from the seventeenth and eighteenth centuries, martyrologies, numerous early German and English language Bibles, and a small collection of fraktur— a folk or vernacular form of decorated manuscript art created by the Pennsylvania Germans primarily between 1740 and 1860.³

Although historians and other scholars regularly utilize these materials for research and several of the objects have undergone conservation treatments, none of the tens of thousands of books and other items in the Special Collections have been subjected to any type of scientific analysis to understand their technology of manufacture or state of preservation. Investigation of the materials used to create works of art using standard analytical chemistry tools (predominately instrumental methods of analysis) enhances and complements an art historical approach. Techniques such as Raman microspectroscopy and x-ray fluorescence spectroscopy (XRF) can be used to identify pigments on works of art and archeological artifacts and are powerful tools to aid in the dating, authentication, conservation, and restoration of these cultural heritage objects. These methods are non-destructive, allow for *in situ* analysis without the need for sampling, and have been used by the authors to examine a variety of cultural heritage objects.⁴

A collaborative project between Juniata and Winterthur Museum was initiated to investigate the Pennsylvania German fraktur in the Special Collections. The identification of the techniques and materials used in the production of these artifacts was intended to enhance our understanding of the fraktur art form and add to Winterthur's growing database on fraktur pigments, paper, and other production information. The analysis and interpretation of these items encompass disciplines that span the arts and sciences: an ideal undertaking at a liberal arts college.

FRAKTUR ART OF THE PENNSYLVANIA GERMANS

The Pennsylvania Germans have long been known for their colorful decorative arts, including works on paper commonly referred to as fraktur. The term is derived from *Fraktur*, a broken or fractured style of writing and the related typeface or font. This style of lettering was used in German-speaking areas of Europe from the beginning of the sixteenth century until World War II and included illuminated manuscripts as well as deeds, contracts, certificates, and other printed forms.⁵



Figure 1. Birth certificate for Maria Meier. Artist unknown, possibly Northampton County, Pa., c. 1765. Umber, indigo, an unknown organic yellow colorant, and iron gall ink on laid paper. 19 x 19 cm. Juniata College Rare Books Collection, MS 70. Photo, courtesy Winterthur Museum.

Decorative motifs were sometimes, although by no means always, added to embellish the documents. German-speaking immigrants brought the fraktur tradition with them to Pennsylvania, where it evolved into a distinctive artistic genre that included both manuscript and printed documents. The most common type of fraktur was the *Geburts-und-Taufschein*, or birth and baptismal certificate, due to the importance of baptism within the Lutheran and Reformed Church to which most Pennsylvania Germans belonged. The Juniata collection contains four such examples in addition to one that documents only a birth (Fig. 1). Probably the earliest fraktur in the collection, it records the birth of Maria Meier on November 12, 1765. No location is specified, but genealogical research has discovered that she may be the Anna Maria Meier who was baptized on November 17 in Hecktown, Northampton County, and identified as the daughter of Martin and Margaret Meier.⁶



Figure 2. Birth and baptismal certificate for Jacob Hüffner. Handwriting and decoration attributed to Daniel Otto on a printed form attributed to Benjamin Meyer, Ephrata, Lancaster County, Pa., c. 1795-98. Vermilion, verdigris, an unknown organic yellow colorant, and iron gall ink on laid paper with watermark "CB" (Christian Bauman, papermaker at Ephrata from about 1793 to 1815). 33 x 39 cm. Juniata College Rare Books Collection, B 1X. Photo, courtesy Winterthur Museum.

As demand for birth and baptismal documents increased during the early 1780s, many artists increasingly turned to printed certificates to help expedite their work. Print shops in Ephrata, Reading, York, Lebanon, and dozens of other towns in southeastern Pennsylvania began producing such forms. During the 1790s, a three-heart format became popular, such as the example that can be attributed to the printshop of Benjamin Meyer before he moved from Ephrata to Harrisburg (Fig. 2).⁷ It records the birth of Jacob Hüffner, son of Valentin and Barbara (Miller) Hüffner, on November 3, 1789, in Huntingdon County. The genealogical data is written in the hand of Daniel Otto (c. 1770-c. 1820), son of fraktur artist Henrich Otto and a prolific artist in his own right. The 1800 census lists Daniel as a resident of Mahoney Township, Northumberland County, but by 1805 he had moved to what is now Rebersburg, Miles Township, Centre County.⁸ Perhaps he stopped in Huntingdon County en route. The colorful decoration on this certificate also appears to be Otto's work and includes a green parrot with red and yellow accents in the upper left corner that is likely a stylized version of the now-extinct Carolina parakeet; the only parrot species native to the eastern United States, these birds were once so plentiful in Pennsylvania that farmers considered them a nuisance.⁹

The next two certificates are unusual in that both were made for Susanna Nelson, born on July 19, 1793, to Johannes and Hanna Nelson in Upper Milford Township, Northampton (now Lehigh) County. One of the certificates is entirely hand-drawn and is likely the earlier of the two (Fig. 3). It is backed with a German-language newspaper dated May 6, 1801 and printed in Sunbury, Northumberland County. The artist is unknown but was clearly inspired by schoolmaster Henrich Weiss, who worked in the Upper Milford area and produced fraktur certificates with similar motifs and layout.¹⁰ This fraktur is in poor condition and in need of treatment to prevent further disintegration. The other certificate (Fig. 4) is a printed form attributed to the shop of Wilhelm Lepper in Hanover, Adams County.¹¹ It is rare to find more than one birth and baptismal certificates do reveal, however, is mobility, as they include elements from several different counties, suggesting that the Nelson family may have moved about or at least had access to objects from disparate places including Hanover and Sunbury, which are nearly 100 miles apart.

The latest certificate in the group was printed by Gustav S. Peters of Harrisburg, who together with Johann Moser began color printing as early as 1825 (Fig. 5).¹² This example records the birth and baptism of Magdalena Guth on November 3, 1830, in Brecknock Township, Lancaster County. It dates from about 1840, when Magdalena was ten years old, and helps document that these pieces were often not made until children had at least survived infancy.¹³ The angels in profile flanking the central text panel were widely used on printed baptismal certificates from about 1806 to 1840, when printers began using angels with a frontal view. This fraktur came to Juniata in 1960 as part of the W. Emmert Swigart rare



Figure 3. Birth and baptismal certificate for Susanna Nelson. Artist unknown, probably Upper Milford Township area, Lehigh County, Pa., c. 1793. Red lead, orpiment, verdigris, and iron gall ink on laid paper. 35 x 42 cm. Juniata College Rare Books Collection, MS 1X. Photo, courtesy Winterthur Museum.



Figure 4. Birth and baptismal certificate for Susanna Nelson. Printed form attributed to Wilhelm Lepper, Hanover, Adams County, Pa., c. 1800. Indigo, vermilion, an unknown organic yellow colorant, and iron gall ink on laid paper with watermark "TK" (unknown). 35 x 42 cm. Juniata College Rare Books Collection, MS 2X. Photo, courtesy Winterthur Museum. books collection.¹⁴ Its whereabouts prior to that time, as well as the provenance of the other four fraktur, is unknown.

A transcription and translation of the five fraktur studied are provided in the Appendix for the benefit of those who do not read German script and are unfamiliar with the phrasing frequently encountered in fraktur. Capitalization and spelling are retained in the transcriptions. Areas on the fraktur with blank spaces that were intended to be filled in with additional data are indicated with underscored lines. Handwritten information, such as names and dates, is shown in bold font.¹⁵

There are two published accounts that describe the analysis of fraktur using the tools of analytical chemistry, thus making it possible to make comparisons and place the results of the present work in a broader context. The first scientific study of the pigments used by Pennsylvania German scriveners/fraktur artists in the creation of their vibrantly colored illuminated manuscripts was published by Carlson and Krill in 1978.¹⁶ Using XRF, they were able to characterize the pigments present in eleven fraktur. In the case of the red pigments, they identified vermilion in eight of the eleven, iron oxide in two of the eleven, and one red lake pigment (an organic dye precipitated onto an inorganic substrate). Prussian blue was identified on six of the eight fraktur that contained blue pigments, and azurite (or the synthetic version known as blue verditer) was identified on one object. The green pigments were found to be equally split between verdigris and green earth, the only exception being one arsenic-based green pigment such as Paris green or Scheele's green. One example of chrome yellow was found, as well as three uses of yellow ochre and two of gamboge resin or another organic yellow. The brown and black pigments were found to be iron-containing, and the white pigments were identified as lead white.

A larger study using both XRF and Raman spectroscopy was carried out by Mass et al in 2003 and 2004.¹⁷ Of the thirty-six fraktur that contained red regions, seventeen were colored with vermilion and sixteen with a mixture of vermilion and red lead. Two were found to contain an iron oxide pigment and one was found to have an organic red colorant. Of the twenty-one fraktur that contained blue paints, fourteen were colored with pure Prussian blue, five with a mixture of Prussian blue and lead white, one with the blue pigment smalt, and two with an organic blue colorant, likely indigo. Of the thirty-five fraktur that contained green pigments, thirty-three were found to be colored with verdigris, one with a green earth, and two with emerald green. The thirty fraktur with yellow pigments contained twenty-two examples of organic yellow pigments, likely gamboge resin, two examples of chrome yellow, two examples of yellow ochre, and four examples of orpiment. The thirty-six fraktur that contained brown and black pigments were found to contain iron gall ink in each case. Iron oxide was also found in three examples.



Figure 5. Birth and baptismal certificate for Magdalena Guth. Printed form by Gustav S. Peters, Harrisburg, Dauphin County, Pa., c. 1840. Vermilion, chrome yellow, and iron gall ink on wove paper. 44 x 33 cm. Juniata College Rare Books Collection, B 2X. Photo, courtesy Winterthur Museum.

ANALYTICAL METHODOLOGY

The analysis and characterization of pigments and dyes on manuscripts is of major significance in cultural heritage research, as it can assist with the dating and authentication of the artwork, as well as inform any necessary conservation treatments and increase our knowledge about the people who

produced it. The scientific study of works of art cannot "prove" a work is genuine, but pigment anachronisms and other anomalies that are not due to undocumented restorations can show a work is likely a fake or forgery. A wide variety of analytical techniques have traditionally been employed in the identification of pigments on art objects. Quite often it is necessary to employ more than one method in order to achieve unambiguous results for all colorants present on an object. XRF and Raman microspectroscopy are commonly used in combination to identify pigments. They are complementary techniques in that the former is an elemental analysis method and the latter can be used to identify specific molecular species. When done properly, both methods are non-destructive and allow for *in situ* analysis of artworks without the need for sampling that would adversely affect the integrity of the manuscript.

Raman microspectroscopy is a type of vibrational spectroscopy that involves the illumination of a sample with monochromatic light and the measurement of the photons that are inelastically scattered that is, scattered with frequencies different from that of the light incident upon the sample. The difference in frequency corresponds to the energy of the stretching and bending motions associated with the molecular structure of the sample. The Raman spectrum (a plot of the frequency of the scattered light in cm⁻¹ versus relative intensity) is characteristic of the material(s) present and can be thought of as a "spectral fingerprint." Comparison with Raman spectra of known pigments allows for the identification of the pigments present in a sample. In a typical setup, low power laser radiation is brought to focus on an individual pigment grain on the artifact via the microscope objective. The Raman scattering by the sample initially retraces the path of the incident light beam, and is then collected by the same objective and directed to the spectrometer and the detector. Raman microscopy is a sensitive and specific technique that offers high spectral ($\leq 1 \text{ cm}^{-1}$) and spatial ($\leq 1 \mu m$) resolution. It can be used to distinguish between materials with different structures but identical chemical formulas (e.g., polymorphs such as calcite and aragonite, which have the same formula—CaCO₃—but different Raman spectra). Some materials, such as organic colorants, display significant fluorescence, and this can significantly obscure the Raman signal, making identification difficult or impossible. The use of an infrared laser (e.g., 785 or 1064 nm) can reduce or largely eliminate this background fluorescence. Representative examples of Raman spectra obtained from the fraktur are shown in Fig. 6.

In x-ray fluorescence spectroscopy, x-rays are directed at a sample, causing the atoms to become ionized as inner-shell electrons are ejected. When an outer-shell electron takes the place of the "hole" left by the core electron, energy is released in the form of x-rays. The emitted x-rays have a lower energy than the incident x-rays and their energies are specific to the energy gaps of electron orbitals of the elements present in the sample. An XRF spectrum consists of a plot of the energy of the emitted x-rays (in KeV) versus relative intensity. More than one emission line is seen for heavy atoms with multiple energy levels.

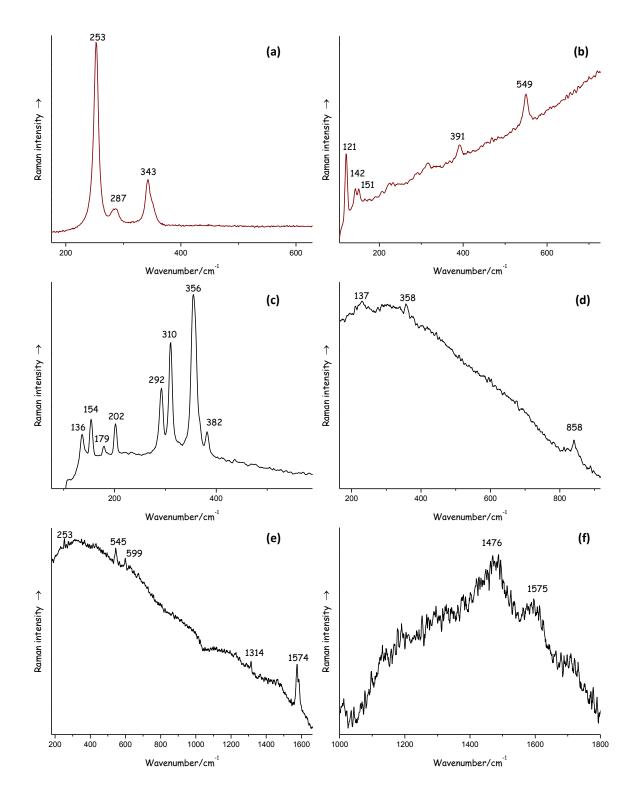


Figure 6. Representative examples of Raman spectra obtained from the Juniata fraktur showing characteristic peaks in wavenumbers (cm⁻¹): (a) vermilion, (b) red lead, (c) orpiment, (d) chrome yellow, (e) indigo, (f) iron gall ink.

XRF is only routinely used to identify elements with mass greater than sodium since the x-rays emitted by lighter elements are lower in energy and are consequently absorbed by the atmosphere. XRF can often be used to determine the relative abundance of elements present in a sample.

XRF is particularly useful when trying to identify materials that do not give good Raman spectra, such as metals or some inorganic compounds (e.g., gold leaf on an illuminated manuscript or umber pigments, which strongly absorb the Raman's incident laser light). In some cases, the color of a pigment combined with its XRF spectrum can be sufficient to identify the material present. For example, a red pigment that is found to contain significant amounts of mercury can be assumed to be vermilion— mercuric sulfide (HgS), while red pigments composed principally of lead are probably red lead—lead(IV) oxide (Pb₃O₄). Since the x-rays penetrate both the pigment and underlying substrate, the spectra of colored areas reflect the elements that are present in both. Though there are often only relatively low levels of inorganic species present in paper and other organic substrates, it is still prudent to analyze an area of the object containing no pigment prior to the paint analysis to determine baseline levels of elements in the substrate. A representative example of an XRF spectrum obtained from one of the fraktur is shown in Fig. 7.

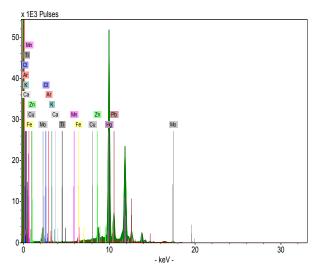


Figure 7. The XRF spectrum from a red flower petal (green spectrum) on the birth and baptismal certificate for Jacob Hüffner (B 1X). Mercury (Hg) is the most abundant element but small amounts of lead (Pb) and zinc (Zn) are present beyond the background levels of copper (Cu), Zn, iron (Fe), Hg, calcium (Ca), potassium (K), titanium (Ti), manganese (Mn) and arsenic (As) found in the paper substrate (shown as the red line). The red pigment is presumed to be composed of mostly vermilion (HgS). The presence of Pb may suggest that some red lead (Pb₃O₄) was mixed with the vermilion.

The analysis of the Juniata fraktur was conducted in the Scientific Research and Analysis Laboratory at Winterthur Museum. XRF was carried out using a Bruker Artax open architecture spectrometer with a molybdenum X-ray tube and a polycapillary focusing optic providing a spot size of approximately 70 microns. The tube parameters were a voltage of 50 kV and a current of 600A. The spectral collection time was 100 seconds. The instrument was energy calibrated against a copper alloy but quantitative values were not determined. Raman microspectroscopy was carried out using a Renishaw inVia spectrometer with a 785 nm laser, a spectral resolution of 3 cm⁻¹, 1200 l/mm diffraction grating, a laser power of 3 mW, a 50X objective, and a spectral range of 100 - 3200 cm⁻¹.

RESULTS AND DISCUSSION

A total of nine pigments were identified on the fraktur with each piece having a simple color palette composed of two to four of these colorants.¹⁸ Each object was analyzed at multiple locations using XRF and Raman microspectroscopy. Table 1 shows the elements identified on each fraktur using XRF. The background level of elements found in the paper was always taken into account when identifying relative amounts of elements present in the XRF spectra of colored areas as well as the ink used for the text. Figure 6 includes representative Raman spectra of the pigments found on the five objects examined. The identification of the pigments was made by comparison with published spectral libraries of pigments.¹⁹ No attempt was made to identify the binder mixed with the pigments on these objects, but fraktur artists typically employed traditional watercolor binders such as gum arabic or cherry tree gum.²⁰ It is usually not possible to determine the identity of such organic binders with XRF or Raman microspectroscopy, but the binder material also does not tend to interfere with the analysis of pigments. The analysis results for the fraktur are described in some detail below.

Color	Meier (MS 70)	Hüffner (B 1X)	Nelson (MS 1X)	Nelson (MS 2X)	Guth (B 2X)	
Paper	Fe, Mn, Ca, K, Ti	Fe, Cu, Zn, Hg, Ca, K, Ti, Mn, As	Cu, Fe, As	Fe, Cu, Ca, K	Ca, Fe, K	
Red	color not present	Hg, Pb	Pb	Hg, Pb	Hg, Pb, Cr	
Yellow	Fe, Ca	Cu	color not present	Cu, Fe, Ca	Pb, Cr, Fe	
Green	color not present	Cu, Hg	Cu	color not present	color not present	
Blue	Fe, Mn, Cu, Pb	color not present	color not present	Ca, K, Fe, Pb	color not present	
Brown	Fe, Mn, Ca, K, Pb, Ti	color not present	As	Fe, Cu, K, As	color not present	
Black	Fe, K	Fe, Cu	Fe, Cu, Pb	Fe, K, Ca	Fe, K	

Table 1. Elements identified on the fraktur using XRF with the major elements shown in bold and the minor elements in regular typeface.

The birth certificate for Maria Meier (MS 70, Fig. 1), the oldest fraktur in the collection, has a simple palette consisting of yellow, blue, and varying shades of brown applied on a piece of laid paper. XRF analysis of the paper substrate showed the presence of iron (Fe), manganese (Mn), calcium (Ca), potassium (K), and a trace amount of titanium (Ti). The faded yellow pigment used for flower petals and lettering is probably an organic colorant since the XRF spectrum showed no additional elements. No Raman spectrum could be obtained for the yellow areas. The faded blue-grey color found in leaves and other decorative elements gave a Raman spectrum with bands at 545, 599 and 1574 cm⁻¹ that are characteristic of the dye indigo $(C_{16}H_{10}N_2O_2)$.²¹ XRF analysis of the blue areas showed small amounts of copper (Cu) and lead (Pb). No Raman spectrum could be obtained from the brown areas on the border and in the flowers, but XRF showed Fe, Mn, K, and Ca, plus a trace of Pb and Ti. The presence of these elements suggests the use of umber, a brown earth pigment containing clay minerals rich in oxidized iron species and manganese (II) oxide (MnO₂).²² The black lines and letters contain high levels of Fe, which suggests the use of iron gall ink—an ink made from ferrous sulfate (FeSO₄) and the gallic acid- and pyrogallin-containing nodules found on oak trees. The Raman spectra of the black areas on this as well as the other fraktur showed a weak, characteristic band for iron gall ink at ~ 1475 cm⁻¹, but the results were not conclusive.²³

The birth certificate for Jacob Hüffner (B1X, Fig. 2) was prepared with red, yellow, and green pigments, and black ink. The object shows damage and had undergone conservation treatment prior to entering the Juniata collection. In some areas, the green paint and black ink have caused deterioration of the paper to the point that losses are evident in the tail feathers of two of the birds, several flower petals, and some of the handwritten letters. In an attempt to consolidate the fraktur and prevent further deterioration, a layer of fine silk (crepeline) was attached to each side of the object, probably with wheat starch paste, at some point in the past. The "silking" process was used as a conservation treatment beginning in the late nineteenth century but has fallen out of favor since silk yellows and becomes brittle with age. This conservation treatment is believed to be the cause of the notable feathering of the ink seen in this fraktur.²⁴ An XRF spectrum of the paper shows the presence of Cu, zinc (Zn), Fe, and mercury (Hg), as well as small quantities of Ca, K, Ti, Mn and arsenic (As). The mercury (Hg) identified in the XRF spectrum of the red pigment is clearly from vermilion (HgS), based on the characteristic bands at 253, 287 and 343 cm⁻¹ in the Raman spectrum.²⁵ In fraktur the presence of Hg together with a small amount of Pb is typically indicative of vermilion mixed with red lead (Pb₃O₄), though no Raman spectrum was obtained corresponding to the latter pigment. The yellow pigment shows Cu and gives only fluorescence in the Raman spectrum. The green pigment used for petals and bird feathers contains high levels of Cu and a trace amount of Hg. Though no bands could be seen using Raman microspectroscopy, the presence of only Cu in a green pigment strongly suggests the use of verdigris

 $(Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2)$.²⁶ The remaining traces of green pigment along the edges of the deteriorated areas of the paper show higher levels of Cu than the paint in the non-affected green spots.

Iron is the main element found in the XRF spectra of both the printed and handwritten black letters. The iron gall ink used for the handwritten portions was either applied more thickly or was prepared with an excess of ferrous sulfate, since the amount of Fe found in these areas is significantly higher than in the printed letters. In either case, the paper has totally disintegrated in the shape of the letters where the ink was applied most heavily since the ferrous ion (Fe^{2+}) is relatively acidic and is known to cause hydrolysis of cellulose fibers. Using XRF it was also possible to document the bleeding of the iron gall ink, presumably as a result of the prior conservation treatment (see Fig. 8). The amount of Fe in the "halo" around the handwritten letters is lower than in the letters themselves but still higher than in the paper substrate.

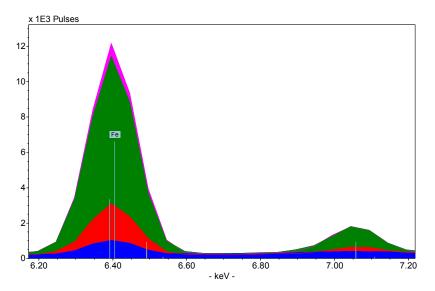


Figure 8. Enlarged area of the XRF spectra from three areas of the letter "s" in the word "sohn" in the birth and baptismal certificate for Jacob Hüffner (B 1X) showing differing levels of Fe. The damaged area (pink) and the undamaged center of the letter (green) have nearly identical levels of Fe. The "halo" around the letter (red) has a lower amount of Fe, but still more than the paper background (blue).

The two birth and baptismal certificates prepared for Susanna Nelson have many differences, including the pigments used to create them. The older, hand-drawn version (MS 1X, Fig. 3) has a palette consisting of red, green, and brown colorants. The red pigment found in the petals contains high levels of lead and gives a Raman spectrum with bands at 121, 142, 151, 391 and 549 cm⁻¹, allowing it to be conclusively identified as red lead (Pb₃O₄).²⁷ The green pigment used for parts of the flowers shows only Cu in the XRF spectrum, suggesting the use of verdigris, although no Raman spectrum could be obtained to confirm this supposition. Unexpectedly, XRF analysis of the light brown areas of the flowers showed

high levels of As. A Raman spectrum showing bands at 136, 154, 179, 202, 292, 310, 356 and 382 cm⁻¹ was obtained that confirmed the presence of As in the form of orpiment (As_2S_3). Though orpiment is frequently thought of as a bright yellow pigment, it can also appear yellowish brown or even golden. It is also possible that the pigment has undergone some degradation and fading over time to produce the light brown color.²⁸ There are dark and light types of text on this fraktur—the dark letters contain the usual high Fe content associated with iron gall ink along with some Pb and Cu, while the lighter text has a significant quantity of Pb and only a small amount of Fe. The eight dark leaves on the periphery of the fraktur contain Fe with some Pb and Cu and have a Raman spectrum suggestive of iron gall ink.

Susanna Nelson's later birth and baptismal certificate (MS 2X, Fig. 4) was made from paper that has only small amounts of Fe, Cu, Ca, and K. The red pigment is composed of mostly Hg and gives a Raman spectrum corresponding to vermilion, though the Pb present in the XRF spectra again suggests a mixture containing red lead. No Raman spectrum could be obtained for the yellow areas on this fraktur, and the XRF spectrum only shows low levels of Fe, Cu, and Ca that are barely above the paper background. The blue pigment found in the flower designs contains Ca, relatively low levels of K and Fe, and a trace of Pb. Though no Raman spectrum could be obtained, this blue may be indigo since other commonly used blue pigments, such as azurite (2CuCO₃•Cu(OH)₂) or Prussian blue (Fe₄[Fe(CN)₆]₃), would have had substantially higher levels of Cu or Fe, respectively.²⁹ The brown leaves and stems of the flowers have Fe and some Cu, K, and As, suggesting that diluted iron gall ink or an iron-containing pigment such as hematite or goethite was used. The XRF spectrum for the inked letters shows high levels of Fe.

The birth and baptismal certificate prepared for Magdalena Guth (B 2X, Fig. 5) is the only fraktur in the collection that was prepared via a color printing process. The yellow pigment used in the border, angels, and birds was analyzed using XRF and found to contain chromium (Cr), Pb, and small amounts of K and Ca. This result, combined with bands at 358 and 838 cm⁻¹ in the Raman spectrum, allowed the pigment to be identified as chrome yellow (PbCrO₄). Chrome yellow is a synthetic pigment that was made available commercially at the beginning of the nineteenth century, so it would have been available for use as a printing ink in c. 1840 when this fraktur is believed to have been printed.³⁰ The red pigment is vermilion, based on the presence of Hg in the XRF spectrum and the characteristic strong band at 254 cm⁻¹ in the Raman spectrum. In fraktur the presence of Hg and Pb together is typically an indication of vermilion mixed with red lead. Iron gall ink is again the ink that was likely used on this fraktur, based on the presence of Fe in the XRF spectra and the weak band at ~1475 cm⁻¹ in the Raman spectrum.

The summary of the pigments found on the objects in the Juniata collection is shown in Table 2. The presence of five pigments (two reds, two yellows, and one blue) could be confirmed by RM, with the

Color	Pigment	Formula	Meier (MS 70)	Hüffner (B 1X)	Nelson (MS 1X)	Nelson (MS 2X)	Guth (B 2X)
Red	Vermilion	HgS		×		×	×
	Red lead	Pb ₃ O ₄			×		
Yellow	Organic yellow	Unknown organic compound, likely gamboge	×	×		×	
	Orpiment	As ₂ S ₃			×		
	Chrome yellow	PbCrO ₄					×
Green	Verdigris	$Cu(C_2H_3O_2)_2$ •2 $Cu(OH)_2$		×	×		
Blue	Indigo	$C_{16}H_{10}N_2O_2$	×			×	
Brown	Umber	Fe and Mn oxides and clay minerals	×				
	Hematite or goethite	Fe oxide or hydroxide				×	
Black	Iron gall ink	FeSO ₄ and oak galls	×	×	×	×	×

 Table 2. Summary of the spectroscopic analysis of pigments identified on each fraktur using a combination of XRF and RM.

identity of the other pigments inferred from the XRF spectra. On the fraktur of Meier, Hüffner, and Nelson (MS 2X), a yellow pigment containing Cu and/or traces of Fe and Ca was identified using XRF. Since there are no common Cu-based yellow pigments, it may be that the yellow is organic in nature and that the Cu or other elements found are due to mixtures with small amounts of other pigments. This yellow may be an organic colorant such as gamboge, a pigment commonly used by fraktur artists.³¹ Umber and verdigris were not detected by Raman microspectroscopy, but these pigments are known to be difficult to identify using only Raman spectroscopy. However, these two pigments are suspected to be the red-brown and green pigments used on several of the fraktur because they were typical pigments of the time period, are known to be used on other fraktur, and Fe/Mn or Cu, respectively, were found via XRF. The complete deterioration of the paper in some of the green areas on the birth and baptismal certificate of Jacob Hüffner is also consistent with the pigment being verdigris (basic copper acetate) as this pigment is known to cause browning and degradation of cellulosic materials.³² Iron gall ink was the ink used on all of the fraktur, both the handwritten and printed text. Fe was not the only metal identified in the black areas because the ferrous sulfate (also known as copperas or blue vitriol) called for in iron gall ink formulas frequently was contaminated with Cu. The increased amount of Cu in the ink on the Hüffner fraktur may also have contributed to the degradation of the paper substrate in some areas. The results of the analyses are consistent with previous spectroscopic studies on the pigments used by fraktur artists.

The Juniata fraktur reveal the use of vermilion and red lead, but used independently rather than the red lead being an adulterant in the vermilion. The use of umber is not surprising since red and yellow ochres were identified in the previous studies. Likewise, the finding of indigo in the blue regions was borne out by both prior studies. The assumption, based on XRF results, that the green pigment found in two of the Juniata fraktur is verdigris is consistent with the predominant use of this pigment in the fraktur previously studied. The use of solely inorganic/mineral based yellow pigments such as orpiment and chrome yellow is unexpected, but the sample set for the Juniata pieces is small, and the three unidentified organic yellow pigments are likely gamboge, based on the results of previous studies. Both orpiment and chrome yellow are well-documented fraktur pigments.

SUMMARY AND CONCLUSIONS

The pigments and ink on five Pennsylvania German fraktur from the Juniata College Special Collections dating from between 1765 and 1840 were analyzed using x-ray fluorescence spectroscopy and Raman microspectroscopy. The combination of scientific analysis and art historical research provided information on the materials that were used to create these interesting pieces as well as their state of preservation. The nine pigments identified on the fraktur are entirely consistent with the colorants typically used by fraktur artists. Two of the fraktur are in poor condition and are in need of immediate conservation. The results of our analysis will inform the approach used to preserve these objects from further degradation. Though the collection is small, it contains some remarkable objects that are representative of the materials and stylistic influences found in Pennsylvania fraktur from the mideighteenth to the mid-nineteenth centuries. This collaborative project has enriched our understanding of the fraktur art form that is a fascinating part of the cultural heritage of Pennsylvania.

ACKNOWLEDGEMENTS

The authors wish to thank Joan Irving, Paper Conservator of Winterthur Museum and adjunct Assistant Professor of the Winterthur and University of Delaware Art Conservation Program, for helpful comments on prior conservation treatments of the fraktur, and the II-VI Foundation for financial support (K.R.H. and R.R.H.).

AUTHORS

Richard R. Hark is a professor of chemistry at Juniata College where he has taught organic chemistry and a "Chemistry of Art" course since 2001. Dr. Hark's research interests include the application of laser-based analytical techniques for the analysis of artworks, archeological artifacts, geomaterials, and items of forensic interest.

Katelyn R. Houston graduated from Juniata College in 2012 with a degree in chemistry (summa cum laude) before entering a doctoral program in chemistry at the University of North Carolina-Chapel

Hill. The analysis of the fraktur owned by Juniata formed a portion of her senior thesis for which she received distinction in her discipline.

Jennifer Mass is a senior scientist and laboratory director at the Scientific Research and Analysis Laboratory (SRAL) at Winterthur Museum and adjunct assistant professor in the Art Conservation Department of the University of Delaware. Her research interests include the materials and techniques of Pennsylvania German painted and inlaid furniture as well as fraktur.

Lisa Minardi is an assistant curator at Winterthur Museum and a specialist in Pennsylvania German fraktur and furniture. She is currently in the planning stages of creating an online fraktur archive that would include images, translations, and catalog entries for thousands of fraktur in both museum and private collections.

Hedwig T. Durnbaugh is the curator of rare books and historical documents at the L.A. Beeghly Library at Juniata College and an expert on the hymnody of German immigrant groups to North America and in contemporary Scandinavian hymnody. She is a lecturer and the author of numerous articles, essays, and translations including *The German Hymnody of the Brethren 1720-1903* (Philadelphia: The Brethren Encyclopedia, Inc., 1986).

John Mumford is the Juniata College Library Director. He has overseen the organization, promotion, and development of the Special Collections and Archives, including preservation, digitization and microfilm projects. He uses the Special Collections in his Introduction to Library Research courses.

APPENDIX

Transcription and Translation of the Fraktur **MS 70** (Fig. 1) [Birth and baptismal record: Maria Meier] [TRANSLATION] 1765 12ten 1765 12th Anno d[omini] Den In the year o[f the Lord] the Dag November day of November Morgends Im in the morning under *Storbion* [i.e. Skorpion] *Ist Die* [the sign of] Scorpio Maria Meierin Maria Meier Geboren. Der Herr was born. The Lord Gebe Ihr Glick und grant her good fortune and Segen Amen blessings. Amen

B IX (Fig. 2)

118 Juniata Voices

[Birth and baptismal record <u>Jacob Hüffner</u>] Diesen beyden Ehgatten, als valentin hüffner Und seiner ehelichen Hausfrau barbara geborne Millern ist ein sohn zur Welt geboren im Jahr Unsers Herrn Jesu 1789 den **3ten Tag Nofember** Um ____ uhr ____ im Zeichen de ____ [TRANSLATION] To these two spouses, Valentin Hüffner and his wife Barbara née Miller a son was born in the year of our Lord Jesus 1789 the 3rd day November at ____ o'clock in the sign of the ____.

Gott gebe Gnad, Kraft, und Stärke, daß dieser **Jacob hüffner** in der Furch des HERRN möge Aufwachsen und zunehmen in grosser Begierde der vernünftigen lautern Milch, das ursprüngliche Heil der Seelen zu suchen,

Nach abgelegten Glaubens=Bekentniß und Erkentniß der Sünde durch wahre Reu und busse vor der Christlichen Gemeinde, zur

Geistlichen Widergeburt der heiligen Taufe befördert, und von Pfarher Waschen Prediger und Diener des Worts, nach Christi Befehl, Matth. 28,19 getauft, in in den Gnaden=Bund

Gottes einver=

Leiben worden Dieser Jacob hüffner ist, als ein Glied in die Gemeinschaft der Hei=

Ligen, durch das Bad der Wiedergeburt und Erneurung des Heiligen Geistes, wie St. Paulus lehret, Titum 3,5.6.7.

und ist auf= und angenommen worden, den ____ *ten Tag*

17 ____ und durch den wahren Glauben an unsern Erlöser Jesu Christo, des so theuer erworbenen Ver= Dienstes der himmlischen Freuden, und der ewigen Seligkeit Erben eingesetzet. Mithin vergiβ nicht wie Der Apostel Paulus, Colosser 1, f.12.14 die Pflicht beschreibet. Saget Dank dem Vater der uns Tüchtig gemacht hat zum Erbtheil der Heiligen im Licht. u.s.w.

Tauf=Zeuge sind vatter und mutter

Dieser Jacob Hüffner

Ist geboren und getauft in Pennsylvania, in

Hontington Caunty in

Taunschip.

[TRANSLATION]

[May God grant grace and strength that this Jacob Hüffner, in the fear of the Lord,

grow up and increase in great desire of the pure milk, to seek after the original blessed state of the soul; after confession of faith and acknowledgment of sin, through true repentance and penitence before the Christian congregation, through

spiritual rebirth of holy baptism be nurtured; and by Pastor Waschen,

preacher and servant of the Word, according to Christ's commandment, Matth. 28, 19 was baptized, and in God's covenant of grace was made a member. This Jacob Hüffner, as a member of the community of saints through the bath of rebirth and renewal of the Holy Spirit, as St. Paul teaches Tit. 3,5.6.7. was received the _____ th day 17 and through the true faith in our Savior Jesus Christ, the dearly earned merit of the heavenly joys and eternal blessed state, heir. Therefore do not forget how the Apostle Paul, Col. 1, v.12.14. describes one's duty. Give thanks to the Father who has made us fit for our inheritance of the saints in the light etc. Witnesses are father and mother This Jacob Hüffner Was born and baptized in Pennsylvania, in Huntingdon County in

township.

[Two stanzas from a well-known German baptismal hymn.]

Ich bin getauft, ich steh im Bunde, I am baptized, I stand united Durch meine Tauf mit meinem Gott with my God through my baptism. So sprech ich stets mit frohem Munde, I therefore always speak joyfully in Kreuz, in Trübsal, Angst und Noth. Ich bin getauft, des' freu ich mich, I am baptized, that's a joy for me. Die Freude bleibet ewiglich. The joy lasts eternally.

Ich bin getauft, ob ich gleich sterbe, Was schadet mir das kühle Grab? Ich weiß mein Vaterland und Erbe, Das ich bey Gott im Himmel hab. Nach meinem Tod, ist mir bereit, Des Himmels Freud= und Feyer=Kleid.

SOLI DEO GLORIA [To God alone the glory]

in hardship, sadness, fear and need.

I am baptized, and when I die, how can the cool grave hurt me? I know my fatherland and legacy that I will have with God in Heaven. After death, Heaven's garment of joy and celebration is prepared for me

MS 1X (Fig. 3) [Birth and baptismal record Susanna Nelson] [ms. copy]

120 Juniata Voices

Susanna Nelsen ist geboren im Jahr nach Christi Geburt 1793 den 19 Julius und hat darauf die heilige Tau fe Empfangen von dem geistigen Herr Pfarrer eschbig und zwar in der Kirche zu ober mühlford daun schip Nortgenton dann sie [?] ist von Christlichen eltern Relion geboren ihr vater hiß Johan Nelson und ihre muter hanna gleinen Taufzeu gen waren Katrina Rodenbergern

[TRANSLATION]

Susanna Nelson was born A.D. 1793 the 19th July and has received holy baptism by the Reverend Pastor Eschbig [Espich] in the church at Upper Milford Township Northampton County, because she was born of Christian parents [into the ...] religion. Her father's name was Johann Nelson and her mother [was] Hanna Glein. Witnesses were Katrina Rodenberger

[Traditional rhymed reflection on youth and aging by Heinrich Schütz (1623).] *Ich bin Jung Gewesen und alt worden...*

MS 2X (Fig. 4)

[Birth and baptismal record <u>Susanna Nelson</u>] [pre-printed form]
Diesen beyden Ehegatten,
als Johannes Nelson und seiner ehelichen Hausfrau Hana eine
geborne Gleimin ist ein Dächterlein zur Welt geboren, wie weiter folgt:
Diese Sussana Nellson ist geboren im Jahr unsers Herrn 1793 den 19 Julyus um 1 Uhr [?]
und getauft den 26 september von Herrn Chri Espig Prediger und Diener des worts nach Christi Befehl,
Matth. 28, 19.
Die Taufzeugen sind Catharina Rotebergern Latiges Stantes
Diese Sussana Nelson ist geboren und getauft in Amerika, in Staate Pennsylvania
Northemton Caunty Obermilfort Taunschipp.
[TRANSLATION]

121| Juniata Voices

To these two spouses,

Johannes Nelson and his wife Hanna,

née Gleim, a little daughter was born as follows:

This Susanna Nelson was born in the year of our Lord 1793 the 19th July at 1 o'clock [?]

and baptized the 26th September by Chri[stian] Espig [Espich], preacher and servant of the word

according to Christ's command, Matt. 28:19

Witnesses are Catharina Roteberger, unmarried.

Susanna Nelson was born and baptized in America, in the State of Pennsylvania

Northampton County, Upper Milford Township.

[Two stanzas from a German hymn on birth and death.]

Wenn wir kaum gebohren werden, ist vom ersten Lebenstritt bis ins kühle Grab der Erden, Nur ein kuz gemeßner Schritt. \ Ach! mit jedem Augenblick gehet unsre Kraft zurück, und wir sind mit jedem Jahr reif genug zur Todtenbahr; \ und wer weiß, in welcher Stunde uns die letzte Stimme weckt: Denn Gott hats mit seinem Munde \ keinem Menschen noch entdeckt. Wer sein Haus nun wohl bestellt, geht mit Freuden \ aus der Welt: Da die Sicherheit hingegen, ew 'ges Sterben kann erregen.

[TRANSLATION]

Scarcely born into the world, it is only a short measured pace from the first step to the cool grave in the earth. $\ O$ with every moment! Our strength diminishes, and with every year we grow more ripe for the bier. $\ And$ who knows in what hour the final voice will awaken us, because God has $\ not$ revealed this to anybody yet. Who tends to his house will depart $\ from$ the world with joy. Because surety, in contrast, can provoke eternal death.

[Two stanzas from a well-known German baptismal hymn.] Ich bin getauft, ob ich gleich sterbe... Ich bin getauft, ich steh' im Bunde...

B 2X (Fig. 5) [Birth and baptismal record <u>Magdalena Guth</u>]

[Two stanzas from a German hymn on birth and death.] Wenn wir kaum geboren warden... O! wer weiβ, in welcher Stunde...

[TRANSLATION]

Geburts= und Tauf=Schein	Birth and Baptismal certificate
Diesen beyden Ehegatten, als Joseph	To these spouses, Joseph
Guth und seiner ehelichen	Guth and his
Hausfrau Barbara eine Tochter von Joseph Horst	wife Barbara, a daughter of Joseph Horst, a
Ist ein Tochter Zur Welt geboren, den 3ten Tag November	a daughter was born the 3 rd day of
November	
im Jahr Unsers Herrn, 18 30. Diese Tochter	in the year of the Lord 1830. This daughter
ist geboren in Brocknach Taunschip in	was born in Brecknock Township in
Lancaster Caunty, im Staat Pennsyl=	Lancaster County, in the State of Pennsyl-
vania in Nord=Amerika, und ist getauft worden	vania in North America, was baptized
und erhielt den Namen Magdalena Guth	and named Magdalena Guth
den Tag im Jahr unsers	the day in the year of our
Herrn, 18 von Hrn	Lord, 18 by Rev

Die Tauf=Zeugen waren: ____

The witnesses at the baptism were:

[Three stanzas from well-known German baptismal hymns.]

Ich bin getauft, ich steh' im Bunde...

Ich bin getauft in deinem Namen...

Ich bin getauft, ob ich gleich sterbe....

NOTES

- 1. See <u>http://www.juniata.edu/projects/currents/redesign2/specialcollections.html</u> for more information and a brief summary of the holdings of the Juniata College Special Collections.
- 2. G. Friedrich, "The A.H. Cassel Collection at Juniata College," *American German Review*, 7 (1941).
- 3. D.F. Durnbaugh, "Abraham Harley Cassel and His Collection," *Pennsylvania History*, 26 (1959): 332-347.
- 4. R.J.H. Clark et al., "Spectroscopic Study of Mural Paintings from the Church of Saint Eulàlia of Unha," Journal of Raman Spectroscopy, 41 (2010): 1128-1134; L. Burgio, R.J.H. Clark and R.R. Hark, "Raman Microscopy and X-ray Fluorescence Analysis of Pigments on Medieval and Renaissance Italian Manuscript Cuttings," Proceedings of the National Academy of Sciences of the United States of America, 107 (2010): 5726-5731; L. Burgio, R.J.H. Clark and R.R. Hark, "Spectroscopic Investigations of Modern Pigments on Purportedly Medieval Miniatures by the So-called 'Spanish Forger," Journal of Raman Spectroscopy, 40 (2009): 2031-2036; L. Burgio et al., "Spectroscopic Investigations of Bourdichon Miniatures: Masterpieces of Light and Colour," Applied Spectroscopy, 63 (2009): 611-620; J. Mass and C. Matsen, "Understanding Silver Hollow Wares of the Eighteenth and Nineteenth Centuries: Is There a Role for X-ray Fluorescence?" The Decorative: Conservation and the Applied Arts. 2012 IIC Congress, Vienna, Austria; F. Casadio et al., "X-ray Fluorescence Applied to Overglaze Enamel Decorative: Conservation and the

Applied Arts. 2012 IIC Congress, Vienna, Austria; A. Heginbotham et al., "An Evaluation of Inter-Laboratory Reproducibility for Quantitative XRF of Historic Copper Alloys," *Proceedings: Interim Meeting of the ICOM-CC Metal WG*, Metal 2010: Charleston, SC; K.U. Knauer et al., "Organic Coatings Found on Tibetan Buddhist Gilt Copper Alloy Statuary at the American Museum of Natural History," *Proceedings: Interim Meeting of the ICOM-CC Metal WG*, Metal 2010: Charleston, SC; J.L. Mass and C. Bisulca, "Revealed, a Lost Illustration by N.C. Wyeth," *Antiques and Fine Art* Summer/Autumn (2010): 222-223; P.A. Halfpenny and J.L. Mass, "Two Converging Perspectives on One Meissen Tureen," *American Ceramic Circle Journal*, XV (2009): 71-78; R. Fuchs and J. L. Mass, "The Declaration of Independence Service," *American Ceramic Circle Journal*, XV (2009): 169-187; J.L. Mass et al., "Deconstructing a 17th c. Collaboration by David Teniers the Younger and Jan Brueghel the Younger Using Confocal Xray Fluorescence Microscopy," *Materials Issues in Art and Archaeology* VIII (2008): 3-18; and A.R. Woll et al., "The Unique History of The Armorer's Shop: An Application of Confocal Xray Fluorescence Microscopy," *Studies in Conservation* 53 (2008): 93-109.

- 5. For an overview of fraktur, see the introduction of Frederick S. Weiser and Howell J. Heaney, *The Pennsylvania German Fraktur of The Free Library of Philadelphia*, vol. 1 (Breinigsville, Pa.: The Pennsylvania German Society, 1976), pp. xiii-xxviii.
- "Pennsylvania, Births and Christenings, 1709-1950," index, FamilySearch (https://familysearch.org/pal:/MM9.1.1/V2FP-8D9 : accessed 18 June 2012), Anna Maria Meier, 1765.
- 7. On this edition, see K. Stopp, *The Printed Birth and Baptismal Certificates of the German Americans* (Mainz, Germany and East Berlin, Pa.: the author, 1997), vol. 2, pp. 172-173.
- 8. On Daniel Otto, see Russell D. Earnest and Corinne P. Earnest, *Papers for Birth Dayes: A Guide to the Fraktur Artists and Scriveners*, 2 vols. (East Berlin, Pa.: Russell D. Earnest Associates, 1989), vol. 2, pp. 588-589.
- 9. Noel F.R. Snyder, *The Carolina Parakeet: Glimpses of a Vanished Bird* (Princeton: Princeton University Press, 2004).
- 10. On Henrich Weiss, see Earnest and Earnest, *Papers for Birth Dayes*, vol. 2, pp. 801-802.
- 11. On this edition, see Stopp, *Printed Birth and Baptismal Certificates*, vol. 2, p. 228.
- 12. Edward L. Rosenberry, "G.S. Peters and His Joseph's Book of Many Colors," *Der Reggeboge: Journal of The Pennsylvania German Society*, 22, (1988): 1-14.
- 13. On this edition, see K. Stopp, *The Printed Birth and Baptismal Certificates of the German Americans* (Mainz, Germany and East Berlin, Pa.: the author, 1998), vol. 3, p. 70.
- 14. W. Emmert Swigart (1883-1949) was the son of William J. Swigart, one of the six original trustees of the College. He graduated from Juniata in 1906 and in 1908 founded Swigart Associates, an insurance and real estate firm based in Huntingdon. The company has expanded since that time and is now known as the Mutual Benefit Group. "W. Emmert" served the College as a trustee from 1922-1926. His rare book collection came to the college in 1960 as a donation from his wife, Elizabeth. In 1962, to enable the secure storage of the College's rare book collection she also funded the Swigart Treasure Room in his honor as part of the original construction of L.A. Beeghly Library.
- 15. For a full translation of common hymns that appear on fraktur, see Frederick S. Weiser and Howell J. Heaney, *The Pennsylvania German Fraktur of the Free Library of Philadelphia*, (Breinigsville, Pa.: Pennsylvania German Society, 1976), vol. 1, pp. xxiii-xxvi.
- 16. J.H. Carlson and J. Krill, "Pigment Analysis of Early American Watercolors and Fraktur," *Journal of the American Institute for Conservation*, 18 (1978): 19-32.
- 17. J.L. Mass, C.R. Matsen and J.H. Carlson, "Materials of the Pennsylvania German Fraktur Artist," *The Magazine Antiques*, September (2005): 128-135.
- 18. See N. Eastaugh, V. Walsh, T.D. Chaplin, R. Siddall, *Pigment compendium, A dictionary and optical microscopy of historical pigments* (London: Elsevier, 2004), pp. xl–416 for general

124 Juniata Voices

information on these and other pigments encountered in works of art.

- I.M. Bell, R.J.H. Clark and P.J. Gibbs, "Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre- approximately 1850 AD)," *Spectrochimica Acta, Part A*, 53 (1997): 2159-2179; L. Burgio and R.J.H. Clark, "Library of FT-Raman Spectra of Pigments, Minerals, Pigment Media and Varnishes, and Supplement to Existing Library of Raman Spectra of Pigments with Visible Excitation," *Spectrochimica Acta, Part A*, 57 (2001): 1491-1521.
- 20. T. Stanley, "The Fraktur: Its History and a Conservation Case Study," *Journal of the American Institute for Conservation*, 33 (1994): 33-45.
- H.G. Schweppe, "Indigo and Woad," in E. West-Fitzhugh, ed., Artists' Pigments: A Handbook of Their History and Characteristics, vol. 3 (New York: Oxford University Press, 1997), pp. 81-107.
- 22. K. Helwig, "Iron Oxide Pigments: Natural and Synthetic," in B. Berrie, ed., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 4 (New York: Oxford University Press, 1997), pp. 39-109.
- 23. A.S. Lee, P.J. Mahon and D.C. Creagh, "Raman Analysis of Iron Gall Inks on Parchment," *Vibrational Spectroscopy*, 41 (2006): 170-175.
- 24. Silking is believed to have been developed in Europe in the late 1890s and was adopted in the early twentieth century in the US—especially at large repositories such as the Library of Congress. Silk laminates become yellow and brittle, and ultimately detach from the paper substrate. Silk is also slightly acidic. The presence of arsenic in the XRF spectra may be associated with the silking process as arsenic was sometimes added as a pesticide in some recipes. The wet application of the starch paste could have contributed to the severe haloing surrounding the heavily inked marks and the smearing of the red pigment and the development of foxing. The moisture also probably exacerbated the penetration of the iron gall ink and verdigris pigments through the paper substrate onto the verso of the fraktur. See S.R. Albro and H.H. Krueger, "The Jamestown Records of the Virginia Company of London: A Conservator's Perspective" (http://memory.loc.gov/ammem/mtjhtml/mtjessay2.html: accessed 23 July 2012) for more information on the silking process and methods to "de-silk" documents.
- 25. R.J. Gettens, R.L. Feller and W.T. Chase, "Vermilion and Cinnabar," in A. Roy, ed., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 2 (London: Cambridge University Press, 1993), pp. 159-182.
- 26. H. Kühn, "Verdigris and Copper Resinate," in Roy, ed., Artists' Pigments, vol. 2, pp. 131-158.
- 27. E. West-Fitzhugh, "Red Lead and Minium," in R. J. Feller, ed., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 1 (London: Cambridge University Press, 1986), pp. 109-139.
- 28. E. West-Fitzhugh, "Orpiment and Realgar," in West-Fitzhugh, ed., *Artists' Pigments*, vol. 3, pp. 47-80.
- 29. R.J. Gettens and E. West-Fitzhugh, "Azurite and Blue Verditer," in Roy, ed., *Artists' Pigments*, vol. 2, pp. 23-36; B. Berrie, "Prussian Blue," in West-Fitzhugh, ed., *Artists' Pigments*, vol. 3, pp. 191-218.
- 31. H. Kühn and M. Curran, "Chrome Yellow and Other Chromate Pigments," in Feller, ed., *Artists*' *Pigments*, vol. 1, pp. 187-200.
- 32. J. Winter, "Gamboge," in West-Fitzhugh, ed., Artists' Pigments, vol. 3, pp. 143-156.
- 33. G. Banik and J. Ponahlo, "Some Aspects of Degradation Phenomena of Paper Caused by Green Copper-containing Pigments," *Paper Conservator* 7 (1982): 3-7.