

Article Multi-Modal, Non-Invasive Investigation of Modern Colorants on Three Early Modern Prints by Maria Sibylla Merian

Olivia Dill, Marc Vermeulen ^(D), Alicia McGeachy and Marc Walton *

The Center for Scientific Studies in the Arts (NU-ACCESS), Northwestern University, Evanston, IL 60208, USA; oliviadill2024@u.northwestern.edu (O.D.); marc.vermeulen@northwestern.edu (M.V.);

alicia-mcgeachy@northwestern.edu (A.M.)

* Correspondence: marc.walton@northwestern.edu

Abstract: Northwestern University's Charles Deering McCormick Library of Special Collections owns three hand-colored copperplate engravings that once belonged to an edition of *Matamorphosis Insectorum Surinamensium* by artist-naturalist Maria Sibylla Merian (1647–1717). Because early modern prints are often colored by early modern readers, or modern collectors, it was initially unclear whether the coloring on these prints should be attributed to the print maker, to subsequent owners or collectors, or to an art dealer. Such ambiguities posed challenges for the interpretation of these prints by art historians. Therefore, the prints underwent multi-modal, non-invasive technical analysis to assess the date and material composition of the prints' coloring. The work combined several different non-invasive analytical techniques: hyperspectral imaging (HSI), macro X-ray fluorescence (MA-XRF) mapping, surface normal mapping with photometric stereo, visible light photography, and visual comparative art historical analysis. As a result, the prints and paper were attributed to a late eighteenth-century posthumous edition of Merian's work while the colorants were dated to the early twentieth century. This information enables more thorough contextualization of these prints in their use as teaching and research tools in the University collection.

Keywords: Maria Sibylla Merian; colored prints; hyperspectral imaging; X-ray fluorescence spectroscopy; photometric stereo; Prussian blue; non-invasive pigment characterization

1. Introduction

Metamorphosis Insectorum Surinamensium, first published by Maria Sibylla Merian (1647–1717) in Amsterdam in 1705, is among the most famous examples of early modern insect imagery. The volume consists of 60 copperplate engravings, designed by Merian, engraved by professional engravers, Pieter Sluyter, Joseph Mulder, and Daniel Stopendael, and printed in Merian's Amsterdam workshop. The original volume was published in Dutch and Latin editions and was sold either containing unadorned engravings or, for an added fee, hand-colored by Merian or her daughters, Dorothea Maria and Johanna Helena [1]. The product of two years of research conducted on site in Suriname, the images in *Metamorphosis* constitute a landmark in the history of scientific imagery. They contain detailed portrayals of the different stages of metamorphosis of insects native to Suriname and they set these depictions of transformation in the insects' botanical habitats. Although *Metamorphosis* contains inaccuracies, embellishments, and mistranslations, the images in the volume as a whole are unique for the depth of information that they provide about the flora and fauna of Suriname, for their vivid yet concise compositions, and, notably for this study, for the fact that they number among few early modern natural history prints to survive with original coloring.

Whether color could be used as reliable and reproducible descriptive feature of natural history specimens was hotly contested amongst early modern botanists, naturalists, and artists [2]. Reproducing the color of natural phenomena, especially in the context of expeditions like Merian's, challenged naturalists to develop means to systematize their



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terms and observations [3] and demanded expertise in art, craft and science, making the valence and materiality of early modern color a rich and active area of research for historians of art and science [4]. Merian herself chose to include color as a significant feature of insects' descriptions. In the texts accompanying her images she was careful to include lively textual descriptions of insects' color as identifying features [5]. In the images themselves she relied on a system of modelli, painted in watercolor on paper and vellum, in order to standardize the colors used to represent insects in colored editions of the prints [1]. *Metamorphosis* constitutes an important case study in the history of early modern colored prints.

The study of color in early modern European woodcuts and engravings poses challenges to print scholars, notably that it is often difficult to assess when and by whom coloring is applied [6]. It was common practice among early modern European print owners or book readers to interact with printed works [7] and to add their own annotations or coloring using ink, watercolor, or gouache [8]. It was also common for dealers and collectors especially in the nineteenth century to add color to prints either as enthusiasts or as forgers [9]. In the case of *Metamorphosis*, these challenges associated with authenticating colored prints more generally are compounded by the fact that Merian's original copper plates survived after her death. They were embellished and reprinted in several posthumous editions in the The Netherlands and France in 1726, 1730 and 1771, thus often making it challenging to assess the proximity of loose-leaf prints to Merian's workshop [10].

Analytical methodologies have been employed in the study of color in early modern works on paper; in particular, X-ray fluorescence (XRF) and multispectral photography have been shown to be effective methods of characterizing colorants used to color prints [9,11,12] and illuminated manuscripts [13]. Some have used art historical and technical analyses (XRF and Raman spectroscopy) to study the relationship between printing and color workshops and practices in the sixteenth and seventeenth centuries [6]. These studies concern themselves with works whose coloring can be verified to be early modern. Some have applied XRF to identify modern coloring on early modern prints [8] but there remains further work to be done in specifying and characterizing the practice and materials of modern coloring of earlier prints. Merian's work in particular has been the subject of some technical analyses, which used microscopic investigation to distinguish between prints and counterproofs but not in order to classify or propose dates for the pigments used [14].

Three painted prints from *Metamorphosis* (Call no. Folio 581.9 S357.m; Figure 1) reside in Northwestern University's Charles Deering McCormick Library of Special Collections. These prints are referenced in Merian's text as plate 9, plate 54 and plate 55 and in the following we refer to individual prints by these in-text plate numbers. The coloring on these prints is carefully done and thickly applied. With the exception of two peppers in plate 55, the color scheme of the Northwestern Special Collection prints follows that of counterproof and watercolor versions of the same images that are securely attributed to the Merian workshop, such as those in the British Museum [15–17]. The care of coloring, as well as the aforementioned factors surrounding the history of colored prints by Merian and others, made it initially unclear when, why, and by whom the Northwestern University Special Collections prints and their coloring were produced. Still, given the significance of *Metamoprhosis* in the histories of botany and entomology and with respect to the eighteenth century use of color in illustrated natural history, these prints represent an invaluable archival resource.



Figure 1. Prints from Maria Sibylla Merian's *Metamorphosis* in Northwestern University Chalres Deering McCormick Special Collections, call no: Folio 581.9 S357.m: plate 55 (**left**), plate 9 (**middle**), plate 54 (**right**).

In order to assess how, why, and by whom the prints were made, and in particular whether they were made by the same maker, the prints in Northwestern Special Collections underwent technical analysis with macro X-ray fluorescence (MA-XRF), hyperspectral imaging, transmitted light photography, and photometric stereo imaging. These data were analyzed in dialogue with archival art historical research to characterize and date three separate components of the prints: pigments, printed lines, and paper support. MA-XRF and, in two cases, hyperspectral data were used to investigate the prints' pigments, photometric stereo imaging was used to investigate how the printed marks were made, and transmitted light photography was used to visualize paper structure. Exhaustive characterization of pigments, including modern organic pigments, may require the use of molecular techniques such as Raman spectroscopy [18–21] or FTIR [22]. While the use of these two techniques would have been ideal in this study, no sampling was possible on these prints, and we did not have access to the necessary portable instrumentation for in situ analyses. Therefore, the investigation of the coloring materials could only be performed using MA-XRF and hyperspectral imaging, the combination of which may give good insights into inorganic colorants but limited insights into organic ones. The analysis of the prints presented here can better contextualize these specific prints, and shed light on whether and how the coloring on these prints may contribute to the study of the eighteenth century use of color in natural history. More broadly, this analysis provides valuable information for characterizing modern coloring of early modern prints and demonstrates the use of a multimodal workflow that combines XRF with other modes of analysis.

2. Materials and Methods

2.1. X-ray Fluorescence Spectroscopy

The prints were fully scanned using the NU-ACCESS MA-XRF system described in [23], for which the X-ray tube and polycapillary optic were replaced by a 50 W transmission Rh anode X-ray tube (Varex Imaging, Salt Lake City, UT, USA) and 500 μ m collimator, respectively. MA-XRF scans were collected with a dwell time of 0.2 s, at 40 kV voltage and 1.250 A current. An XGLabs Elio X-ray fluorescence spectrometer operating at 40 kV and 600 μ A was used to collect spot samples for comparison and confirmation. All XRF data processing to create elemental distribution maps was done in Python with the PyMCA framework [24].

2.2. Hyperspectral Imaging (HSI)

Hyperspectral images of the prints were acquired using a Resonon Pika II hyperspectral camera measuring between 400 and 900 nm with 2 nm spectral resolution. Only data between 410 and 900 nm were used for identification due to noise affecting lower wavelength channels. Hyperspectral data analysis was performed using the method and code provided in [25]. The method uses the Uniform Manifold Approximation and Projection (UMAP) algorithm to reduce the dimension of spectral data and then clusters hyperspectral data to produce characteristic spectra, called endmembers, for each color in each print.

2.3. Photometric Stereo Imaging

All three prints were imaged with a photometric stereo dome that is constructed of 81 LEDs, mounted at regular intervals on the concave interior of a hemispherical dome [26]. The prints were placed under the dome and illuminated with each LED in sequence while one photograph was captured for each incident lighting angle. Captures were made with a Canon EOS 50 Mark III DSLR fitted with a 20 mm prime lens. Data were processed using the near lighting model described in [26] and using open source software provided therein to produce three-dimensional false color maps indicating the orientation of the prints' surface (i.e., normal maps).

2.4. Transmitted Light Imaging

Watermarks are thinner regions of antique laid paper that when viewed in transmitted light appear lighter than the surrounding fibers. Early modern paper manufacturers placed watermarks into their papers by weaving of patterns into the wires of the screen-like molds used to shape paper sheets. Here, transmitted light images of the prints were captured in order to better visualize any watermarks within the sheets. After slipping a light sheet between each print and its mat as described in [27], one photograph was taken in ambient light and another with the print illuminated from below with the light sheet. A weighted subtraction of the two images was performed using the algorithm outlined in [28] in order to increase the visibility of watermark data within the sheets. Captures were made with a Canon EOS 50 Mark III DSLR, fitted with a Canon Zoom Lens EF 24–105 mm and with a Daylight Wafer 2 LED light table (model number D/E/U/A 35030).

3. Results and Discussion

3.1. Pigments

We propose the use of certain pigments on the basis of qualitative observation of MA-XRF maps, hyperspectral distribution maps and associated characteristic reflectance curves. In the case of Prussian blue and cadmium red the extraction of representative spectra from hypserspectral maps supported the identification of pigments. The earliest known manufacturing dates for potential pigments (Table 1) were used to propose *terminus post quem* for the prints. XRF data can be used to calculate elemental concentrations and therefore quantitatively identify the presence of certain elements; however, in our case approximate identifications were sufficient to address research questions concerning the prints' provenance. Summaries of all proposed identifications are given in Appendix A and data supporting this study are available in the associated supplementary information file.

Table 1. Earliest known date of commercial availability for pigments used to date the prints in NU

 Special Collections.

Pigment	Earliest Known Date
Prussian blue	1724 [29]
Cadmium red	1919 [30]
Cadmium barium red	1926 [31]
Cadmium yellow	1818 [30]
Lithopone	1878 [32]
Titanium white	1920 [33]

3.1.1. Brown

High pixel intensities in iron and manganese XRF maps in brown regions suggest the use of brown umber in both prints [34–36]. The co-ocurrence of iron and manganese is observed most clearly in the pomegranate husk in plate 9 and chrysalis on plate 55 (Figure 2). Umber was available to artists long before the eighteenth century and its use does not rule out an early modern date for the coloring [35]. However, high pixel intensities in XRF maps for cadmium and sulphur in brown and dark yellow regions of plate 9 suggest the presence of cadmium yellow, either mixed with brown umber or applied in a separate layer. Cadmium yellow's earliest use as an artist's pigment is 1818 [30].



Figure 2. MA-XRF maps for cadmium (left), iron (center), and manganese (right) in plate 9 (top) and plate 55 (bottom).

3.1.2. White

High pixel intensities in the titanium MA-XRF map suggest the use of titanium white in white regions of plate 55, such as the white flower (Figure 3) [33,37]. Titanium white was not commonly available as an artist's pigment before around 1920, thus moving the *terminus post quem* for the coloring on plate 55 to the first quarter of the twentieth century [33]. Characteristic features in reflectance data for titanium white fall between 393 and 406 nm, which is outside the range of the hyperspectral camera used for this study [38,39]. Therefore in our case HSI is not useful in confirming this identification.



Figure 3. Visible light photograph and (left) and MA-XRF map for titanium in Plate 55 (right).

High pixel brightness in XRF maps for zinc, barium and sulphur occurred in several regions of all three prints (Figure 4). This combination is consistent with the use of lithopone, which consists of zinc sulfide and barium sulphate [32,40]. Lithopone is a white pigment, but is observed here in regions that visually appear green and blue, suggesting its use as a filler. Lithopone was first patented and commercially produced in 1878; thus, its presence on these prints further confirms that the coloring on the prints is modern [32]. The use of two whites may suggest the use of two campaigns of coloring, or the choice to differentiate areas of the print.



Figure 4. False color images indicating brightness in the XRF maps for Ba_L, S_K, and Zn_k in plates 9 (**left**) 54 (**center**) and plate 55 (**right**).

3.1.3. Red

High pixel brightness in cadmium, sulphur, and selenium XRF maps in several red regions of plates 54 and 55 (Figure 5) suggests the use of cadmium red to color red regions in both prints [30,41]. Characteristic spectra in hyperspectral data Figure 6) are consistent with those for cadmium red [30,41] namely the inflection point around 590 nm and absorption maximum around 500 nm. Cadmium red became commercially available in 1919, confirming the early twentieth century *terminus post quem* for the coloring [30].



Figure 5. False color images indicating brightness in the XRF maps for Cd_L, S_K, and Se_K, in plates 54 (**left**) and plate 55 (**right**).



Figure 6. Characteristic spectra for unidentified green (**left**) and cadmium and barium-rich reds (**right**).

Additionally, we observe that in the upper left-most pepper of plate 55 and in the uppermost spike of the flower on plate 54, circled in red in Figure 7, pixel intensities in cadmium XRF maps are a factor of 4 lower than the pixel intensities in other red regions of the cadmium map of the same print. The pixel brightness for selenium is also low in these areas and barium remains constant throughout. Because visibly the red remains consistent, it is possible that in these regions a second red, possibly an organic red with a barium-rich substrate, such as barium oxide, was applied in addition to cadmium red [31].

Pixel brightness is low in all regions of the Selenium XRF map for Plate 9 (Figure 8), indicating that cadmium red was not used in Plate 9. Cadmium and barium are found together in red regions of plate 9 (Figure 7), suggesting the use of cadmium barium red [30,42] in plate 9 or possibly, as in plates 54 and 55, a barium-rich organic red. The presence of multiple reds could indicate multiple distinct campaigns of coloring or the choice to distinguish or retouch parts of the prints. The shared use of cadmium red between plates 54 and 55 suggests that both were produced using a shared palette.



Figure 7. Details from plate 55 (**left**), plate 9 (**center**), and plate 54 (**right**) showing XRF maps for barium and cadium.



Figure 8. Visible light photograph and (left) and MA-XRF map for selenium in plate 9 (right).

3.1.4. Blue

The analysis of hyperspectral data suggests the use of Prussian blue in plate 9. The characteristic spectral curve in blue regions (Figure 9), in particular the local minimum around 675 nm and the inflection point around 554 nm, are consistent with characteristic spectra for Prussian blue published in other identifications of Prussian blue [43–45]. Prussian blue did not become commercially available until 1724, seven years after Merian's death, confirming that the coloring could not have been applied during Merian's lifetime [29].

Although Prussian blue is rich in iron, an element that can be detected with XRF, it has been observed that in practice Prussian blue requires relatively little pigment to produce strong coloration and thus it can be challenging to detect this pigment with XRF [25,46]. In our case we observe high pixel intensities in MA-XRF maps for iron in regions corresponding to darker shades of blue in the butterfly at the upper right of plate 9 (Figure 9). All blue regions of the butterfly's blue wings in hyperspectral images of plate 9 demonstrate the characteristic reflectance spectrum of Prussian blue, which together with the iron map allows us to confirm the identification of Prussian blue.



Figure 9. Details from MA-XRF map for iron (**top left**), blue endmember map (**bottom left**) and characteristic spectra (**right**) used to identify Prussian blue in plate 9.

3.1.5. Green and Yellow

We were unable to propose the presence of specific colorants in the case of a number of likely-organic green and yellow pigments. The hyperspectral data treatment was able to extract characteristic spectra for green regions, but these curves did not correspond to the curves for inorganic pigments [47]. XRF data in these regions did not register elements typically associated with green pigments (such as copper) or inorganic yellows (such as iron). This lack of association along with the identification of barium, sulphur, zinc, and, in some green regions, iron with varying pixel brightness throughout suggests the use of unidentified organic pigments or mixtures. Sampling and invasive analysis would be necessary to further specify these pigments.

3.1.6. Comparisons between Prints

The recurrence of several pigments (lithopone, barium-rich and cadmium reds, and brown umber) identified on the basis of XRF data and, in the case of cadmium red and Prussian blue, hyperspectral imaging suggest that there is a common palette between the three prints. This is supported by the close correspondence in hyperspectral data and characteristic spectra between prints. Characteristic spectra for red regions of plate 54 and plate 55, which conform to published spectra for cadmium red (Figure 6), support the identification of the same pigment in both prints [30,32]. Although we are unable to precisely identify which pigment they correspond to, characteristic spectra for the green regions in each print are nearly identical between the three plates (Figure 6), suggesting the repeated use of one green pigment between all three. The use of the same pigment between prints suggests that they were colored together by the same hand or with a systematic application of color between the three.

3.2. Printed Lines

Normal maps and comparison with other printed editions of *Metamorphosis* were used to determine whether lines that appeared to be printed were in fact the product of an eighteenth century intaglio printing process such as copperplate engraving, or if they were outright forgeries or reproductions.

3.2.1. Photometric Stereo Normal Maps

In normal maps for all three prints produced through photometric stereo data, a large-scale deformation of the sheet within the region of the plate mark can be observed (Figure 10). Because this deformation only occurs within the plate mark indicating the boundary of the copperplate we propose that these deformations resulted from the application of high pressure to a wet sheet during printing. Smaller-scale deformations in the surface were more difficult to register due to the thickness with which the paint is applied



to the surface, but in plate 54 the printed lines are raised from the surface of the sheet (Figure 10), thus supporting the proposition that these were printed via an intaglio process.

Figure 10. Magnitude of the normal direction along the horizontal axis for plate 54 (**left**) and detail (**right**).

3.2.2. Comparison with Other Editions

Prints in Northwestern University were compared to other editions of Merian's *Metamorphosis*: an edition published in Amsterdam by Merian in 1705 in the University of Chicago Special Collections (call no.: ff QL466.M57 1705), a 1726 edition published in Amsterdam by P. Gosse in Northwestern Medical School's Galter Health Sciences Library (call no.: XO 595.7 M54d 1726) and a 1771 edition translated into French published in Paris by LC Desnos (call no.: XO 595.7 M54h3 1771), also in Galter Health Sciences Library. All three editions are uncolored.

After visual inspection of plates from different editions it was observed that Northwestern Special Collections' prints have a Roman numeral plate number in the upper right of each print and a French name for the plant species at the bottom of each print. These two features are unique to the 1771 edition, *Histoire Generalé des Insectes de Surinam...*, which is the last known edition of Merian's work, published in Paris in 1771 by L.C. Desnos (Figure 11) [10]. The presence of printed features that are only present in the 1771 edition confirms that the NU Special Collections prints may be attributed to a 1771 edition.



Figure 11. Details from plate 54 from Galter Library's 1726 edition (**left**), NU Special Collections (**center**) and Galter Library's 1771 edition (**right**). A Roman numeral plate number in the upper right and a label in French were added to the plates between 1726 and 1771.

3.3. Paper

If documented in watermark databases, watermarks can provide information about the date and location of the paper production. Computed watermark images show that Plates 9 and 55 share a watermark in the shape of a bishop or abbot, wearing a mitre and a cross, bearing a staff and banner (Figure 12). The dark shadow around vertical chain lines indicates that the paper is antique laid paper, rather than laid or wove, suggesting that it was produced before the end of the eighteenth century [48].



Figure 12. Computed images of watermarks found in plate 55 (**top left**), plate 9 (**top middle**) and plate 54 (**bottom**). The outline of a bishop watermark can be observed when manually reinforced in plate 9 (**top right**).

Dating of the watermarks themselves was inconclusive. This particular bishop watermark has not been documented in any of the common databases of eighteenth century watermarks, and does not match with watermarks in other editions of *Metamorphosis*, given in Figure 13.



Figure 13. Transmitted light images showing watermarks in different editions of *Metamorphosis*. 1705 (not shown) and 1726 (**left**) editions both share the Strasbourg Lily watermark. The 1705 countermark is "PVL" (not shown) the 1726 countermark is "Honig" (**middle**). The 1771 edition has an unidentified watermark (**right**) and unintelligible countermark with text.

Watermarks are helpful, however, in addressing whether sheets were produced and procured from the same maker or edition. Plates 9 and 55 have the same watermark; however, the prints were impressed on the opposite side of the sheet with the watermarks vertically inverted with respect to one another. This suggests that these two sheets come

from the same batch of paper and are likely mold-mates. This supports the hypothesis that plates 9 and 55 came from the same original source.

4. Conclusions

This paper has presented the technical analysis of three prints from *Metamorphosis* Insectorum Surinamensium by Maria Sibylla Merian in Northwestern University Library's Special Collections. The analysis was undertaken in order to determine a date, printer, and colorist for the prints, which were difficult to ascertain due to the complexities of the timeline of publication of Merian's works and the common practice of later coloring of early modern prints. This study employed a holistic analysis that would facilitate the non-invasive characterization of the artworks in three layers: pigment, print, and paper. Because of similarities in pigments—brown umber, barium-rich red, cadmium red, and lithopone—used in multiple plates, similar characteristic spectra for green pigments in all three plates, and the matching watermarks in plates 9 and 55 we conclude that the prints belonged to the same edition and were colored together. The use of two different red pigments, one barium-rich and the other cadmium red, and two different white pigments, titanium white and lithopone, alludes to the possibility of multiple campaigns of coloring, but this remains an open question. We date the coloring to post-1920, based on the use of cadmium red and titanium white, which were not commercially available to artists before 1919 and 1920, respectively. Based on the presence of features that are only present in posthumous editions of Merian's plates as they were reprinted in later editions, namely a Roman numeral plate number and French caption, we date the prints themselves to a French translation published in Paris in 1771. A more specific dating of the printed elements or the painted components would require further analysis of the organic components of the drawing and further research into the provenance of the watermarks.

The relative chronology of the different components of the prints in Northwestern Special Collections confirms that the prints are the product of a twentieth century art dealer or collector adding coloration to earlier prints. The dating of the coloring as well as the care with which it was undertaken suggest that this may have been an attempt to add value to relatively low-value later editions of Merian's works. As a result of this study the prints will be re-cataloged in the Northwestern Library catalog and the use of these prints by students and researchers will therefore be better contextualized in terms of this more complicated provenance.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/heritage4030088/s1, Figure S1: Elemental maps resulting from MA-XRF scan of plate 9, Table S2: Results of XRF point analysis for plate 9, Figure S2: Sample locations for XRF point analysis of plate 9, Figure S3: Endmember maps resulting from hyperspectral imaging for plate 9 and associated reflectance spectra, Figure S4: Elemental maps resulting from MA-XRF scan of plate 54, Table S3: Results of XRF point analysis for plate 54, Figure S5: Sample locations for XRF point analysis of plate 54, Figure S6: Endmember maps resulting from hyperspectral imaging for plate 54 and associated reflectance spectra, Figure S7: Elemental maps resulting from MA-XRF scan of plate 55, Table S4: Results of XRF point analysis for plate 55, Figure S8: Sample locations for XRF point analysis of plate 55, Figure S9: Endmember maps resulting from hyperspectral imaging for plate 55, Table S4: Results of XRF point analysis for plate 55, Figure S8: Sample locations for XRF point analysis of plate 55, Figure S9: Endmember maps resulting from hyperspectral imaging for plate 55 and associated reflectance spectra.

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Appendix A. Proposed Pigment Identifications and Corresponding Elements

Color	Elements Present	Possible Pigment
Red	Ba, Cd, S, Si, Zn	Organic red (inferred) with barium substrate, or cadmium-barium red
Yellow	Ba, Cd, Fe, Mn, S, Si, Zn	Brown umber and/or cadmium yellow, lithopone
Green	Ba, Fe, Mn, S, Si, Zn	Organic green (inferred) or Prussian blue mixture, lithopone
Green	Ba, Fe, S, Si, Ti, Zn	Organic green (inferred), or Prussian blue or iron oxide mixture, titanium white, lithopone
Mint Green	Ba, S, Ti, Zn	Organic green (inferred), titanium white, lithopone
Blue	Ba, Fe, Mn, S, Si, Zn	Prussian blue possibly with iron oxide, lithopone
Brown	Ba, Ca, Cd, Fe, Mn, S, Si, Zn	Brown umber, cadmium yellow, lithopone
Paper	As, Ba, Co, Cu, K, Mn, Ni, S, Si	Paper
Mat	Ca, Fe, Ti	Mat

Table A1. Summary of elements present in XRF analysis for plate 9.

Table A2. Summary of elements present in XRF analysis for plate 54.

Color	Elements Present	Possible Pigment
Red 1	Ba, Cd, S, Se, Si,Ti, Zn	Cadmium red, lithopone
Red 2	Ba, Cd, S, Si, Zn	Cadmium red, and/or organic red (inferred) with barium substrate
Pink	Ba, S, Zn	Organic red (inferred), zinc white or lithopone
Yellow 1	Ba, S, Zn	organic yellow (inferred), lithopone
Yellow 2	Ba, Cd, Fe, S, Ti, Zn	titanium white, cadmium-based yellow, lithopone
Light Green	Ba, Fe, S, Ti, Zn	organic green (inferred), titanium white, possibly Prussian blue mixture, lithopone
Green	Ba, Ca, Fe, S, Si, Ti, Zn	Titanium white, organic green(inferred) or possibly Prussian blue mixture, lithopone
Brown	Ca, Fe, Mn, S, Zn	Brown umber
Paper	As, Co, Cu, Fe, K, Mn, Ni, S, Si	Paper
Mat	Ca, Fe, Ti	Mat

Table A3. Summary of elements present in XRF analysis for plate 55.

Color	Elements Present	Possible Pigment
Red 1	Ba,Cd, S, Se, Si, Zn	Cadmium red, lithopone
Red 2	Ba, Cd, K P, Si,	Organic red (inferred) with barium substrate and/or cadmium red
Yellow	Fe	Iron Oxide
Dark Green	Ba, Fe, Mn, S, Si, Zn	Organic green (inferred), or mixture with Prussian blue, lithopone
Light Blue	S, Si, Ti, Zn,	Organic Blue (inferred) mixed with titanium White
Brown	Ba, Fe, Mn, S, Si, Zn	Brown umber, lithopone
White	Si, Ti	Titanium white
Paper	As, Cu, K, Mn, S	Paper
Mat	Ca, Fe, P, Ti	Mat

References

- 1. Reitsma, E. *Maria Sibylla Merian & Daughters: Women of Art and Science;* Rembrandt House Museum: Amsterdam, The Netherlands; JPaul Getty Museum: Los Angeles, CA, USA; ZwolleWaanders: Zwolle, The Netherlands, 2008; pp. 184–204.
- 2. Freedberg, D. The Failure of Colour. In *Sight & Insight: Essays on Art and Culture in Honour of E.H. Gombrich at 85*; Onians, J., Ed.; Phaidon Press: London, UK, 1994; pp. 245–263.
- 3. Lack, H.W.; Ibáñez, V. Recording colour in late eighteenth century botanical drawings: Sydney Parkinson, Ferdinand Bauer and Thaddäus Haenke. *Curtis's Bot. Mag.* **1997**, *14*. [CrossRef]
- 4. Baker, T.; Dupré, S.; Kusukawa, S.; Leonhard, K. (Eds.) Early Modern Color Worlds; Brill: Leiden, The Netherlands, 2016.
- Merian, M.S. Metamorphosis insectorum Surinamensium, ofte Verandering der Surinaamsche Insecten, Waar in de Surinaamsche Rupsen en Wormen Met Alle Des zelfs Veranderingen na Het Leven Afgebeeld en Beschreven Worden...; Gerard Valck: Amsterdam, The Netherlands, 1705; pp. 9, 49, 53.
- Dackerman, S. Painted Prints: The Revelation of Color in Northern Renaissance & Baroque Engravings, Etchings, & Woodcuts; Baltimore Museum of Art: Baltimore, MD, USA; Pennsylvania State University Press: University Park, PA, USA, 2002; pp. 1–9, 49–80.
- 7. Schmidt, S.K.K. Altered and Adorned: Using Renaissance Prints in Daily Life, 1st ed.; Art Institute of Chicago: Chicago, IL, USA, 2011.
- 8. Stillo, S.E. Putting the World in Its "Proper Colour": Exploring Hand-Coloring in Early Modern Maps. J. Map Geogr. Libr. 2016, 12, 158–186. [CrossRef]
- Dackerman, S.; Primeau, T. The History and Technology of Renaissance and Baroque Hand-couloured prints. In *The Broad Spectrum: Studies in the Materials, Techniques, and Conservations of Color on Paper*; Salvesen, B., Stratis, H.K., Webber, P., Wheeler, M., Eds.; Archetype: London, UK, 2002; p. 78.
- Schmidt-Loske, K. Die Tierwelt der Maria Sibylla Merian (1647–1717): Arten, Beschreibungen und Illustrationen; Number 10 in Acta Biohistorica; Basilisken-Presse: Marburg, Germany, 2007; pp. 128–130.
- 11. Hahn, O.; Oltrogge, D.; Bevers, H. Coloured Prints of the 16th Century: Non-Destructive Analyses on Coloured Engravings from Albrecht DÜrer and Contemporary Artists. *Archaeometry* **2004**, *46*. [CrossRef]
- 12. Zannini, P.; Baraldi, P.; Aceto, M.; Agostino, A.; Fenoglio, G.; Bersani, D.; Canobbio, E.; Schiavon, E.; Zanichelli, G.; De Pasquale, A. Identification of colorants on XVIII century scientific hand-coloured print volumes. *J. Raman Spectrosc.* **2012**, *43*. [CrossRef]
- 13. Ricciardi, P.; Legrand, S.; Bertolotti, G.; Janssens, K. Macro X-ray fluorescence (MA-XRF) scanning of illuminated manuscript fragments: Potentialities and challenges. *Microchem. J.* 2016, 124, 785–791. [CrossRef]
- 14. Schrader, S.; Turner, N.; Yocco, N. Naturalism under the Microscope: A Technical Study of Maria Sibylla Merian's "Metamorphosis of the Insects of Surinam". *Getty Res. J.* 2012, 4. [CrossRef]
- 15. Merian, M.S. Red Maize-Like Flower, Possibly a Banana Plant, from an Album of 91 Drawings Entitled 'Merian's Drawings of Surinam Insects'; Reference No. SL,5275.54; British Museum: London, UK, 1701.
- 16. Merian, M.S. Sweet Pepper with Examples of a Butterfly, Chryslais and Caterpillar, from an Album of 91 Drawings Entitled 'Merian's Drawings of Surinam Insects'; Reference No. SL,5275.55; British Museum: London, UK, 1701.
- 17. Merian, M.S. *Two Blue Butterflies and a Caterpillar, from an Album of 91 Drawings Entitled 'Merian's Drawings of Surinam Insects';* Reference No. SL,5275.9; British Museum: London, UK, 1701.
- Casadio, F.; Daher, C.; Bellot-Gurlet, L. Raman Spectroscopy of cultural heritage Materials: Overview of Applications and New Frontiers in Instrumentation, Sampling Modalities, and Data Processing. In *Analytical Chemistry for Cultural Heritage*; Mazzeo, R., Ed.; Topics in Current Chemistry Collections; Springer International Publishing: Cham, Switzerland, 2017; pp. 161–211. [CrossRef]
- 19. Bersani, D.; Madariaga, J.M. Applications of Raman spectroscopy in art and archaeology. J. Raman Spectrosc. 2012, 43. [CrossRef]
- 20. Saverwyns, S. Russian avant-garde... or not? A micro-Raman spectroscopy study of six paintings attributed to Liubov Popova. *J. Raman Spectrosc.* **2010**, *41*. [CrossRef]
- 21. Fremout, W.; Saverwyns, S. Identification of synthetic organic pigments: The role of a comprehensive digital Raman spectral library. *J. Raman Spectrosc.* **2012**, *43*. [CrossRef]
- 22. Prati, S.; Sciutto, G.; Bonacini, I.; Mazzeo, R. New Frontiers in Application of FTIR Microscopy for Characterization of Cultural Heritage Materials. *Top. Curr. Chem.* **2016**, *374*, 26. [CrossRef]
- 23. Pouyet, E.; Barbi, N.; Chopp, H.; Healy, O.; Katsaggelos, A.; Moak, S.; Mott, R.; Vermeulen, M.; Walton, M. Development of a highly mobile and versatile large MA-XRF scanner for in situ analyses of painted work of arts. *X-ray Spectrom.* 2020. [CrossRef]
- 24. Solé, V.A.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectrochim. Acta Part At. Spectrosc.* 2007, *62*, 63–68. [CrossRef]
- Vermeulen, M.; Smith, K.; Eremin, K.; Rayner, G.; Walton, M. Application of Uniform Manifold Approximation and Projection (UMAP) in Spectral Imaging of Artworks. *Spectrochim. Acta Part Mol. Biomol. Spectrosc.* 2021, 252. [CrossRef]
- 26. Huang, X.; Walton, M.; Bearman, G.; Cossairt, O. Near light correction for image relighting and 3D shape recovery. In Proceedings of the 2015 Digital Heritage, Granada, Spain, 28 September–2 October 2015; pp. 215–222. [CrossRef]
- 27. Ruiz, P.; Raju, G.; Dill, O.; Cossairt, O.; Walton, M.; Katsaggelos, A. Visible Transmission Imaging of Watermarks by Suppression of Occluding Text or Drawings. *Digit. Appl. Archaeol. Cult. Herit.* **2017**, *15*, e00121. [CrossRef]
- 28. Boyle, R.D.; Hiary, H. Watermark location via back-lighting and recto removal. Int. J. Doc. Anal. Recognit. 2009, 12. [CrossRef]
- 29. Berie, B.H. Prussian Blue. In Artists' Pigments: A Handbook of Their History and Characteristics; Fitzhugh, E.W., Ed.; National Gallery of Art: Washington, DC, USA, 1986; Volume 3, pp. 191–219.

- 30. Fiedler, I.; Bayard, M. Cadmium Yellows, Oranges, and Reds. In *Artists' Pigments: A Handbook of Their History and Characteristics*; Feller, R.L., Ed.; National Gallery of Art: Washington, DC, USA, 1986; Volume 1, pp. 65–109.
- 31. Barium Oxide—CAMEO. Available online: http://cameo.mfa.org/wiki/Barium_oxide (accessed on 15 May 2021).
- 32. Capua, R. The Obscure History of a Ubiquitous Pigment: Phosphorescent Lithopone and Its Appearance on Drawings by John La Farge. J. Am. Inst. Conserv. 2014, 53. [CrossRef]
- 33. Laver, M. Titanium Dioxide Whites. In *Artists' Pigments: A Handbook of Their History and Characteristics*; Fitzhugh, E.W., Ed.; National Gallery of Art: Washington, DC, USA, 1986; Volume 3, pp. 295–357.
- D'Elia, E.; Buscaglia, P.; Piccirillo, A.; Picollo, M.; Casini, A.; Cucci, C.; Stefani, L.; Romano, F.P.; Caliri, C.; Gulmini, M. Macro X-ray fluorescence and VNIR hyperspectral imaging in the investigation of two panels by Marco d'Oggiono. *Microchem. J.* 2020, 154, 104541. [CrossRef]
- 35. Helwig, K. Iron Oxide Pigments; natural and synthetic. In *Artists' Pigments: A Handbook of Their History and Characteristics;* Anderson, B.H., Ed.; National Gallery of Art: Washington, DC, USA, 1986; Volume 4.
- Laclavetine, K.; Boust, C.; Clivet, L.; Le Hô, A.S.; Laval, E.; Mathis, R.; Menu, M.; Pagliano, E.; Salmon, X.; Selbach, V.; et al. Non-invasive study of 16th century Northern European chiaroscuro woodcuts: First insights. *Microchem. J.* 2019, 144, 419–430. [CrossRef]
- 37. Duran, A.; Franquelo, M.L.; Centeno, M.A.; Espejo, T.; Perez-Rodriguez, J.L. Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy. *J. Raman Spectrosc.* **2011**, *42*. [CrossRef]
- Pronti, L.; Felici, A.C.; Ménager, M.; Vieillescazes, C.; Piacentini, M. Spectral Behavior of White Pigment Mixtures Using Reflectance, Ultraviolet—Fluorescence Spectroscopy, and Multispectral Imaging. *Appl. Spectrosc.* 2017, 71. [CrossRef]
- Picollo, M.; Bacci, M.; Magrini, D.; Trumpy, G.; Tsukada, M.; Kunzelman, D. Modern White Pigments: Their Identification by Means of non Invasive Ultraviolet, Visible and Infrared Fiber Optic Reflectance Spectroscopy. In *Modern Paints Uncovered*, *Proceedings from the Modern Paints Uncovered Symposium, Tate Modern, London, UK, 16–19 May 2006*; Tate Modern: London, UK, 2007; pp.129–139.
- 40. Burnstock, A.; Reissner, E.; Richardson, C. Analysis of Inorganic Materials from Paintings and Watercolours by Paul Cézanne from the Courtauld Gallery Using Two Methods of Non-Invasive Portable XRF with Light Microscopy and SEM/EDX Spectroscopy. In Proceedings of the 9th International Conference on NDT of Art, Jerusalem, Israel, 25–30 May 2008; p. 10.
- 41. Paulus, J.; Knuutinen, U. Cadmium colours: Composition and properties. Appl. Phys. A 2004, 79, 397–400. [CrossRef]
- 42. Rogge, C.E.; Epley, B.A. Behind the Bocour Label: Identification of Pigments and Binders in Historic Bocour Oil and Acrylic Paints. *J. Am. Inst. Conserv.* 2017, *56*, 15–42. [CrossRef]
- 43. Biron, C.; Mounier, A.; Bourdon, G.L.; Servant, L.; Chapoulie, R.; Daniel, F. A blue can conceal another! Noninvasive multispectroscopic analyses of mixtures of indigo and Prussian blue. *Color Res. Appl.* **2020**, 45. [CrossRef]
- 44. Vermeulen, M.; Leona, M. Evidence of early amorphous arsenic sulfide production and use in Edo period Japanese woodblock prints by Hokusai and Kunisada. *Herit. Sci.* **2019**, *7*, 73. [CrossRef]
- 45. Vermeulen, M.; Muller, E.; Leona, M. Non-Invasive Study of the Evolution of Pigments and Colourants Use in 19th-Century Ukiyo-e. *Arts Asia* 2020, *50*, 103.
- 46. Glinsman, L.D. The practical application of air-path X-ray fluorescence spectrometry in the analysis of museum objects. *Stud. Conserv.* **2005**, *50*. [CrossRef]
- Aceto, M.; Agostino, A.; Fenoglio, G.; Idone, A.; Gulmini, M.; Picollo, M.; Ricciardi, P.; Delaney, J.K. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. *Anal. Methods* 2014, 6. [CrossRef]
- 48. Hunter, D. Papermaking: The History and Technique of an Ancient Craft; Dover: New York, NY, USA, 1978.