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HERBERSTEIN'S *GRATAE POSTERITATI* (1560) IN PTUJ AND BRNO: COMPARISON OF THE COLOURING MATERIALS USED ON WOODCUTS

Zusammenfassung

Der Artikel präsentiert einen Vergleich der Elementzusammensetzung von Farbstoffen, die für handgefärbte Holzschnitte in der Ptuj und Brno Kopie des Herberstein Buchs benutzt wurden. Gedruckt wurden sie 1560 in Wien und werden gegenwärtig in der Ivan Potrč-Bibliothek in Ptuj und in den Moravian Provincial Archiven in Brno aufbewahrt. Die in der Ptuj Kopie verwendeten Pigmente wurden durch die PIXE Methode analysiert, für die Brno Kopie wurde die XRF Methode benutzt. Die Methoden sind zwar unterschiedlich, dennoch eignen sich beide um Metall-Ionen in Farbstoffen auf Pergament und auf Papier zu erkennen. Die Ergebnisse zeigen die Verwendung von vergleichbaren Pigmenten, jedoch wurden individuelle Unterschiede zwischen beiden festgestellt.

Keywords: Sigismund von Herberstein, Ptuj, Brno, PIXE, XRF, colouring materials, elemental composition

Introduction

This paper presents a comparison of the elemental composition of colouring materials used on the woodcuts in the Ptuj and Brno copy of Herberstein's book *Gratae posteritati*, printed in Vienna in 1560 and currently kept in the Ivan Potrč Library in Ptuj and in the Moravian Provincial Archives in Brno. The book is a crucial contribution to the diplomatic and political history of 16th-century Europe.[1] In addition to the Latin copy in Ptuj and the German copy in Brno, another seven (Latin and German) copies are known to exist. Other than the Ptuj copy, two more Latin hand-coloured copies exist in London.[2] As far as is known, only the Ptuj copy has serious damage due to iron gall and copper pigments combined with long-term exposure to humidity.

The Ptuj copy *Gratae posteritati* is kept in the Ivan Potrč Library in Ptuj (a second edition of the work, printed by Raphael Hoffhalter in Vienna in 1560[3]). In the past, it formed part of the Herberstein family

1 D. Zadravec, 'Rodbina Herberstein in njen najznamenitejši član Žiga baron Herberstein/The Herberstein Nobility and Its Most Prominent Member, Sigismund von Herberstein', in: *Gratae posteritati: študijska izdaja* (Ptuj: Knjižnica Ivana Potrča – Maribor: Umetniški kabinet Primož Premzl, 2014), 232-233.

2 Two hand-coloured copies of Hoffhalter's Latin edition from 1560 are in London, one at the Victoria and Albert Museum (shelfmark: 86.B.67) and the other in the British Museum in London (Grenville Library, G. 7215).

3 The first edition was published in 1558.

legacy.[4] The Ptuj copy consists of printed text and illustrations. The textblock consists of 120 pages (i.e., 60 leaves arranged in 15 quires[5]), measuring 281 × 179 mm. The binding (290 × 187 × 13 mm) in red velvet is not contemporary. The textblock edges were trimmed considerably in the past, probably when the book was rebound in the late 19th or early 20th century. Due to serious damage, conservation treatment was necessary.[6] The illustrations comprise two prints of the Herberstein family's coat of arms (page 2r coloured and page 61r black and white), six etchings (pages: 6v, 7v, 8v, 10r, 10v, 19v, and one woodcut (page 11v) depicting the profiles of prominent European leaders of the time, six full-page woodcut portraits of Sigismund von Herberstein[7] in ceremonial garb (pages: 8r, 9v, 12v, 14v, 18r, 18v) and two smaller woodcuts (8v and 17v).[8] Detailed descriptions are presented elsewhere.[9]

The Brno copy of the Herberstein autobiography is the German version, printed in Vienna in 1560 by Raphael Hoffhalter[10] and kept in the Moravian Provincial Archives in Brno.[11]

The Brno copy also consists of printed text on paper with hand-coloured illustrations, but the structure of the printed text and the illustrations differ from those of the Ptuj copy.

The textblock consists of 26 leaves arranged in 7 quires – biniums (280 × 190 mm). The binding cover (285 × 205 × 14 mm) is in brown tanned leather decorated (blind-tooled) with the central oval decoration, which was gilded. The textblock edges were not trimmed as at the Ptuj copy, and the book was probably rebound, but the date is not known. The illustrations comprise one print of the Herberstein family's coat of arms (fol. 1r), six full-page woodcut portraits of Sigismund von Herberstein in ceremonial garb (fols. 11r, 12r, 15v, 16v, 19r, and 20v), seven profiles of prominent European leaders of the time, seated figures of the Turkish Sultan Suleyman and the Russian Tsar Wasil, three coloured scenes from travels, a coloured picture of a Turkish camp, a coloured picture of Russian sleds (all on the fol. 23r) and the map of Moscovia dated 1557 (fols. 25r and 26v).

Working method

For the analysis of the elemental composition of colouring materials used in the hand-coloured woodcuts of the two copies of Herberstein's book, two analytical methods were applied: proton-induced X-rays (PIXE[12]) for the Ptuj book and X-ray fluorescence (XRF[13]) for the Brno book.

4 In the Middle Ages, the Herberstein nobility had an immense impact on the history of the area between the Alps, the Danube River, the Adriatic, and far beyond. They indirectly contributed to the current image of this part of the world and society through audacious military activities, intellectual engagement, and scientific and artistic achievements.

5 A quire (or gathering): a group of folded leaves; quires sewn together with other quires form a textblock.

6 The first conservation treatment in 1986/86 and the second in 2013 – SI ARS CKR Ev.n.: 12/107.

7 Sigismund von Herberstein (*Vipava/Slovenia 1486–†Vienna 1566), humanist, polyglot, cosmopolitan, and diplomat in the service of the Habsburg dynasty. He had a brilliant career and contributed greatly to the social advancement of his family. His most popular work (published in Latin, German, and Italian) is *Notes on Muscovite Affairs*, printed in Vienna 1549 and 1557, Venice 1560, Basel 1551 and 1563, and Antwerp 1557.

8 A detailed structural analyses of the copy and a schematic presentation of the conservation treatment are presented elsewhere. J. Vodopivec, 2014: 256–274 and J. Vodopivec, Ž. Šmit, H. Fajfar, 2016: 48 – 57.

9 J. Vodopivec et al., 'Ptujski Gratae posteritati, 1560: struktura, materiali, poškodbe in posegi/The Gratae Posteritati Edition Stored in Ptuj, 1560: Structure, Materials, Damage, and Conservation and Restoration Work', in: *Gratae posteritati: študijska izdaja* (Ptuj: Knjižnica Ivana Potrča – Maribor: Umetniški kabinet Primož Premzl, 2014), 256-276.

10 P. Vidmar, 'Diplomat in njegova imenitna oblačila: ilustracije v Herbersteinovih Gratae Posteritati /The Diplomat and His Valuable Robes: Illustrations in Herberstein's Gratae Posteritati', in: *Gratae posteritati: študijska izdaja* (Ptuj: Knjižnica Ivana Potrča – Maribor: Umetniški kabinet Primož Premzl, 2014), 235.

11 Moravsky zemský archiv v Brně, G 140, 2908(83/a, Vlastni životopis sv. P. z. Herbersteina avtobiografija.

12 PIXE: Proton Induced X-ray Emission. The application of PIXE to organic objects is possible for the analysis of objects composed of organic materials with inorganic components as impurities or additives, and for the analysis of surface layers such as inks, pigments, and all sorts of inorganic inclusions or impurities.

13 XRF: X-ray Fluorescence Analysis. This method is based on the emission and detection of so-called characteristic

The Ptuj illustrations were measured on 26 August 2014 using proton-induced X-rays (PIXE), using the in-air proton beam of the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana. A detailed description is presented elsewhere.[14]

XRF analysis of the Brno illustrations was performed on 8 November 2017 using a laboratory micro-XRF device constructed at the Czech Technical University in Prague. A detailed description of the micro-XRF setup is presented elsewhere.[15]

In both cases (Ljubljana and Prague), the same amount of points in the same places in the Ptuj copy and the corresponding points in the Brno copy were analysed.

Results and discussion

The two books (Ptuj and Brno) differ in the structure of the textblock and in the arrangement of the illustrations. (Figs. 1a–4b) In both of them, all six full-page hand-coloured woodcuts depicting Herberstein in ceremonial garb are present. As a result, we were able to draw a comparison of these six full-page woodcuts in both copies. Due to limitations of space, we present here just four illustrations and the comparison of the results of the analyses of the elemental composition of the colouring materials in the Ptuj and Brno copies.

Fig. 1a: Ptuj, page 8r, white and grey background

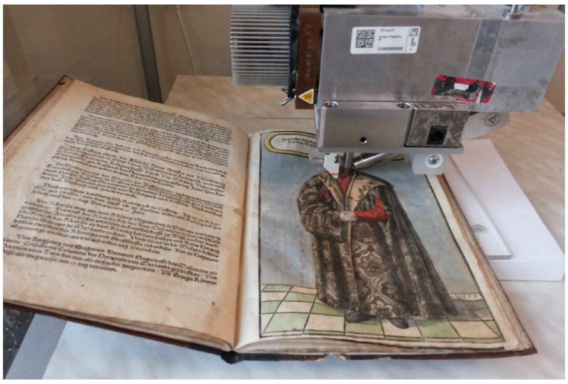
Fig. 1b: Brno, page 11r, light blue background

Fig. 2a: Ptuj, page 12v, long brown-black mantle, pink and grey background


Fig. 2b: Brno, page 15v, long brown-black mantle, pink background

X-rays. XRF is, due to its non-destructiveness, often used for analyses of cultural heritage objects; it is suitable for composition analysis of inks and pigments based on the detection of the present inorganic elements.

14 J. Vodopivec et al., 'Characterisation of Colouring Agents in Determining the Causes of Damage in the Ptuj Gratae Posteritati', in*: Konserviranje knjig in papirja 2 = Book and paper conservation 2* (Ljubljana: Archives of the Republic of Slovenia, 2016), 48-57, cit. 51-55.

15 T. Trojek, 'Reduction of surface effects and relief reconstruction in X-ray fluorescence microanalysis of metallic objects', in: *J. Anal. At. Spectrom.,* 26 (2011), 1253-1257.

Fig. 3a: Ptuj, page 18r, brown-black stocking, light blue background

Fig. 3b: Brno, page 19v, black stocking, intense green background

Fig. 4a: Ptuj, page 18v, light green background

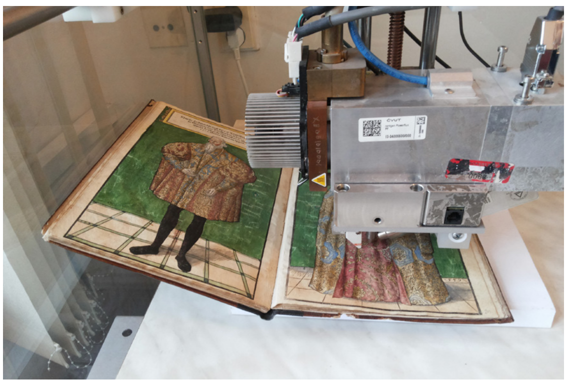

Fig. 4b: Brno, page 20r, intense green background

PIXE analysis of the dyes and pigments in the colouring materials used in the Ptuj copy

The ***white*** pigment, sampled from points 12, 20 (Fig. 2a), 21, and 25 (Fig. 3a), is characterized by a high lead content (>300 μg/cm²), which implies the use of basic lead carbonate.[16] It was also used in combination with other pigments to obtain a lighter cast, such as pale violet (point 18, Fig. 2a) and in the tones used to portray skin colour (points 27, 30, and 36; Figs. 3a-4b).

A **strong red** colour was achieved with cinnabar[17] (sampled from points 2, 8, and 24), while minium[18] was used for milder red tones (point 16). In some cases, a small amount of minium was also mixed with the strong red of cinnabar (points 8 and 24). The dark red in point 31 (Fig. 4a) was achieved by a mixture of pigments: the presence of sulphur and arsenic suggests realgar[19] or auripigment,[20] while the other strong colourants[21] in point 32 (Fig. 4a) are cobalt and iron.[22]

Iron is the most abundant colourant in the **black-brown** tones. In points 2, 6, 9, 10 (Fig. 1a), 14, 19 (Fig. 2a), 29 (Fig. 3a), and 35 (Fig. 4a), it appears together with copper and potassium, and in point 22 with potassium only. This indicates the presence of iron gall ink as a colourant.[23]

The ***green*** colour (sampled from points 4, 7, 11, 17, 23), and 33 (Fig. 4a) is based on copper compounds. As the copper value dramatically exceeds those of other elements, the pigment was probably prepared from malachite[24] or verdigris.[25]

16 Basic lead carbonate: $2PbCO_3 \cdot Pb(OH)_2$

17 Cinnabar: HgS

18 Minium: Pb_3O_4

19 Realgar: α-As_4S_4

20 Auripigment: As_2S_3

21 Colourant: a dye, pigment, or other substance that colours something.

22 J. Vodopivec et al., note 14, 54.

23 J. H. Hofenk de Graff, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs* (Riggisberg: Abegg-Stiftung, 2004), 286.

24 Malachite: $CuCO_3 \cdot Cu(OH)_2$

25 Verdigris is not a unique chemical substance but it is a collective name for various copper acetates. Their color varies from blue to green.

Four points in the ***blue*** fields were measured, and these were found to have three different compositions. The high copper density in point 13 may indicate a pigment-based on azurite.[26] Another blue in point 3 shows no characteristic elements and could have been made of an organic pigment. Two points, 26 (Fig. 3a) and 32 (Fig. 4a), show high densities of silicon, potassium, iron, cobalt, and arsenic; the respective area densities differ by a factor of 1.4, so they represent the same pigment. Nickel appears as a trace element. The pigment is probably a mixture of smalt (potassium and cobalt silicate) and some other copper-bearing minerals, such as erythrite,[27] or (as there is nickel present) skutterudite or asbolane,[28] as well as some other cobaltiferous compound. In either case, this blue pigment appears to be the most specific among the whole colour palette, as demonstrated by the linear relation between arsenic, cobalt, iron, and silicon. It may then be used as a parameter for discriminating between different phases of pigment colouring based on natural cobalt-arsenic minerals in use since the 16th century.[29] The use of synthetic cobalt compounds may be excluded. The production of cobalt arsenate as cobalt violet started only in 1859.[30] In points 26 and 32, a characteristic mineral mixture is present.

Of the three ***yellow*** points, two (points 5 and 34) show no characteristic elements, so they could be organic in matter, while a third (point 28, Fig. 3a) shows a clear signal of gold, which means that the pigment was made of a fine gold powder dispersed in a binder. However, the gold density is low.

The ***skin colour*** was measured in two points in the hands (point 27 and 30, Figs.: 3a, 4a) and in one point on the face (point 36). The predominant element is lead. The skin colour was obtained with a mixture of lead white and red minium, which was enhanced by a small amount of cinnabar in points 27 and 36.

Results of the XRF analysis of the dyes and pigments in the colouring materials used in the Brno copy

As the aim of this study is to compare the elemental composition of the colouring materials in the Ptuj and Brno copies, we focus mainly on the evaluation of similar corresponding points measured in both copies.

XRF analysis of the ***white*** colour (points no. 12, 20, 21, and 25, fig. 3a) identified a pigment containing a high amount of lead (between 200 – 1200 μg/cm²), which signifies the possible presence of lead white. Similarly to the Ptuj copy, in some of the measured points lead white was also applied together with other pigments in order to create a pale shade, either in a mixture or as overlapping (such as the light blue colour in point 13 or light orange in point 27).

Cinnabar was predominantly used in the ***red*** colour (points no. 2 and 24). A more complex structure of the colour layers was found in point 8 (red sleeve with yellow decoration), where a high content of lead, mercury, and gold was found. In this point, cinnabar was probably mixed with some lead pigment (e.g., minium) and this layer was covered with a thin gold surface layer.

XRF analysis of the ***black-brown*** colour showed a varied composition of the pigment used. In point 1, the measured spectrum corresponded to the spectrum of the blank paper, which implies the use of some organic pigment (and thus not identifiable by XRF). In point 10 (brown shoe, Figs. 1a,

26 Azurite: $2CuCO_3 \cdot Cu(OH)_2$

27 Erythrite or red cobalt is a secondary hydrated cobalt arsenate mineral with the formula ($Co_3(AsO_4)_2{\cdot}8H_2O$). Erythrite and annabergite ($Ni_3(AsO_4)_2{\cdot}8H_2O$) (nickel arsenate) form a complete series with the general formula $(Co,Ni)_3(AsO_4)_2{\cdot}8H_2O$.

28 Asbolane is a type of a hexagonal mineral containing calcium, cobalt, hydrogen, manganese, nickel, and oxygen. Its chemical formula is usually given as $(Ni,Co)_{2-x}Mn^{4+}(O,OH)_4 \cdot nH_2O$

29 J. Perez-Arantegui et al., 'Characterization of cobalt pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry', in: *Talanta*, 74, 2008: 1276.

30 R. Hudoklin, *Tehnologija materialov, ki se uporabljajo v slikarstvu. 2. del: slikarska barvila, veziva in redčila* (Ljubljana: Akademija za likovno umetnost UL, 1958), 71.

1b), a high amount of gold was found (120 μg/cm^2) together with mercury, lead, copper, and potassium, so this point was probably coloured with a mixture of pigments covered with a thin gold layer. Arsenic and sulphur were detected in point 19 (long black mantle, Fig. 2b), which may be explained by the use of realgar[31] or orpiment (auripigment)[32]. No iron and copper were detected, which implies the use of carbon black[33] as the colouring material.

Analysis of the ***green*** areas [points no. 7, 11, 33 (figs. 4a and 4b), and 37] revealed a prevailing presence of copper, which suggests the utilization of green pigments (malachite or verdigris. Various shades of green colour in these points were probably achieved by an uneven use of the lead white pigment, because a diverse signal of lead was also detected in the green points. In point 26 (green, Fig. 3b), a high amount of copper (773 μg/cm^2) was detected.

Furthermore, the ***blue*** areas in the Brno copy turned out to have a diverse pigment composition. Results of the XRF analysis in point 3 are similar to the Ptuj copy: no typical element (apart from a small signal of copper) was detected, which may signify the use of an organic pigment. Point 13 showed a high amount of lead and only a very small signal of copper; this may indicate the use of an organic blue pigment applied together with the lead white to obtain a pale blue shade. Elemental composition in point 32 is in agreement with the Ptuj copy; high amounts of silicon, potassium, iron, cobalt, and arsenic were found, and a small amount of nickel (6 μg/cm^2) was also detected in this point. Thus, similar pigments as in the Ptuj copy were probably used in this part (as described in the PIXE Results section).

XRF analysis of the ***yellow*** colour was performed in point 28 (Fig. 3a), where a presence of lead and copper was detected as well as a small amount of gold (similarly to the Ptuj copy). The last compared colour was ***skin colour*** (light orange*)* measured in points 27 and 30. In both points, high contents of lead were determined suggesting that lead white together with minium were used in these points. The considerable signal of mercury in point 27 also revealed the probable presence of cinnabar. (Figs. 3a, 3b, 4a, 4b).

From the analysis of the elemental composition of colouring materials in woodcuts of the two copies of Herberstein's book, the main pigments were determined. The results of PIXE and XRF analyses of the colouring materials are in many cases similar. The ***white*** colour in both books was identified as a pigment containing a high amount of lead, which signifies the presence of lead white.

Cinnabar was predominantly used in the ***red*** colour, but at some point, cinnabar was mixed with some lead pigment (e.g., minium).

The presence of lead (Pb) and copper (Cu) was detected in the ***yellow*** colour as well as a small amount of gold (Au). In the ***skin colour*** (light orange), a mixture of lead white with minium or cinnabar was used.

Analysis of the ***green*** areas confirms the presence of copper, which indicates the utilization of malachite or verdigris. In the ***blue*** points of both the Ptuj and Brno copies, high amounts of silicon, potassium, iron, cobalt, and arsenic and a small amount of nickel were found.

The main difference is in the ***black*** parts. In the Ptuj copy, iron is the most abundant colourant in the black-brown tones. In the Brno copy, nearly no iron and copper were detected by XRF on black mantel (Fig. 2b) and black stocking (Fig. 3b), which indicate that probably black carbon was used as a colouring material.

Conclusion

Although the majority of analysed pigments were practically similar in both books, the physical condition of the two books is

31 Realgar: α-As_4S_4, is an arsenic sulfide mineral.

32 Orpiment: a deep-colored, orange-yellow arsenic sulfide mineral with formula As_2S_3.

33 Black carbon: pure carbon (soot, lamp black), produced by burning organic material.

different. The main apparent difference in the used colourants of the Ptuj and Brno copies was found in the black hue used for colouring the black mantel and black stocking and the intense green background.

The Ptuj copy shows damage resulting from frequent use and long exposure to humidity. In addition to this damage, the hand-coloured illustrations have also suffered due to corrosive action of the iron and copper found in black, green, and blue pigments used. This chemical damage was accelerated by the poor environmental storage conditions, in which the Ptuj book was previously kept.

The book stored in the archives in Brno is well-preserved. The copy shows no significant damage, although the pigments used were similar, except those used for black hue, for which we presume that carbon black was used. For more precise information on the pigments and colours used, an investigation with Raman spectroscopy and FTIR for organic compounds is needed. It would also be interesting to compare the results from the Ptuj and Brno copies with those obtained from the copies kept in London at the V&A Museum and the British Library.

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