Berliner Beiträge zur Archäometrie, Kunsttechnologie und Konservierungswissenschaft

Band 23

Berlin 2015

Rathgen-Forschungslabor
Staatliche Museen zu Berlin

Herausgeberin:
Dr. habil. Ina Reiche
Rathgen-Forschungslabor, Staatliche Museen zu Berlin –
Stiftung Preußischer Kulturbesitz
Schloßstraße 1 a
14059 Berlin

Redaktionsassistentin:
Sabrina Buchhorn
Rathgen-Forschungslabor, Staatliche Museen zu Berlin –
Stiftung Preußischer Kulturbesitz

Herstellung:
Buch- und Offsetdruckerei H. Heenemann GmbH & Co. KG
Bessemerstraße 83 – 91
12103 Berlin
Printed in Germany

ISSN: 0344-5089

Inhalt

Prussian Silk Dyeing in the 18th Century – Scientific Analysis of the Colourants

Jens Bartoll

Stiftung Preußische Schlösser und Gärten Berlin-Brandenburg (SPSG), Abteilung Restaurierung, Naturwissenschaftliches Labor, P. O. Box: 601462, 14414 Potsdam, Germany

Abstract

A large number of original silk textiles from the second half of the 18th century have been preserved in the collection of the Prussian Palaces and Gardens Foundation. Dyestuff analysis of 36 objects of this collection was carried out using High-Performance Liquid Chromatography (HPLC) among other methods. The results provide an insight into the praxis of Prussian silk dyeing that developed rapidly under the reign of Frederick II. The Prussian palette of dyestuff is compared to the one recommended in the written historical sources of that time.

The Prussian dyers used not only the most common and durable dyes such as cochineal, indigo, weld or dyer's broom, but also some dyes with poor light fastness as for example brazilwood, safflower and orchil. This was necessary in order to create all the colours fashionable at that time. The mixtures of the dyes were often "fine tuned" and quite complex and can be seen as proof of the Prussian silk dyers's craftsmanship.

1 Introduction

Decorative silks were an important part of the interior of European royal palaces in the 18th century. The European silk industry – including silk dyeing – was still dominated by France in the first half of the 18th century. Frederick II of Prussia, who came to power in 1740, was passionate about the development of an advanced Prussian silk industry in order to avoid expensive imports (Evers 2014). Therefore he recruited experienced craftsmen from all over Europe, for example from France, Italy, Switzerland or Holland (Nicolai 1769, Schmoller & Hintze 1892, Fidicin 1858). The silk dyers Plantier from France and Thomas Persani from Italy were among the first who settled in Berlin and Potsdam. The international experts were expected to train the local craftsmen. By order of the king buildings were erected in Berlin and Potsdam to house dye factories (Schmoller & Hintze 1892, Fidicin 1858, Martin 1989).

Figure 1: "Rotes Tressenzimmer" (red braid room) of the prince's lower chambers in the New Palace, Potsdam Sanssouci with original wall covering (Brothers Baudouin and sons, Berlin, 1766–68). The red damask was dyed with cochineal. Photo: W. Pfauder SPSG.

The chroniclers of the 18th century disagreed about the quality of the Prussian silk dyeing industry. On the one hand in 1769 and 1786 Nicolai attested the silk dyeing manufactories in Berlin a good and even splendid state (Nicolai 1769, Nicolai 1786). Johann Friedrich von Pfeiffer on the other hand – who personally inspected Prussian silk dyeing factories in the second half of the 18th century – judged differently. According to his writings from 1780, the Prussian silk dyeing industry suffered from the absence of clear regulations and a deficit in the scientific exploration of the bases of dyeing (von Pfeiffer 1780).

Fortunately, many decorative silks dyed in Prussia in the second half of the 18th century have survived in the collection of the Prussian Palaces and Gardens Foundation (figure 1). Among them are damasks, colourful patterned fabrics and brocades that had formerly decorated walls and furniture in the royal palaces in Berlin and Potsdam.

The collection has been studied in detail for the first time during the last five years by a team of art historians, restorers and scientists, culminating in the preparation of a collection catalogue (Evers et al. 2014). Thus it was possible to examine the materials and techniques that were actually used by the Prussian silk dyers and to evaluate the quality of their products. The collection can be seen as a representative sample of the Prussian silk industry of the second half of the 18th century, as the Prussian king was one of the main customers for these luxury goods.

The results of this examination were also used to answer questions about dating and provenance of the silks as well as recognising conservational problems, such as changes in colouration.

This article will concentrate on the scientific analysis of the colourants of 36 dyed silk objects of the Prussian collection. More detailed art historical and technical information for each object can be found in the catalogue (Evers et al. 2014). The analytical findings will be compared with written historical sources.

2 Historical sources

There were a number of publications on silk dyeing available in Prussia in the 18th and the beginning of the 19th centuries.

French scientists such as Charles François de Cisternay du Fay (1698–1739), Jean Hellot (1685–1766), Pierre Joseph Macquer (1718–1784), Claude Louis Berthollet (1748–1822) and Jean-Baptiste Vitalis (1759–1832) were among the first who studied the scientific bases of dyeing. Their writings became international standard works on this subject and were often also translated into German. Apparently, there were only a few scientists in Germany interested in this field, for example Carl Wilhelm Pörner (1732–1796) in Meißen, Johann Beckmann (1739–1811) in Göttingen or Sigismund Hermbstädt (1760–1833) in Berlin (Hofenk de Graaff 2004).

Hermbstädt, a technical writer, pharmacist, and chemist wrote a well-known textbook on dyeing in 1802 (Hermbstädt 1802). In general, his writings represent a valuable source for dyeing in Prussia, as the author lived and taught in Berlin for a long time and his knowledge combined practical and theoretical aspects of the subject. Furthermore, he had a deep insight into Prussian economic policy. For example, in his book from 1802 he listed important dyeing materials ("… indigo, cochineal, safflower, woad, gallnuts, sumac, and different dyewoods, roots, and barks; … tartar, saltpetre, lemon juice, verdigris, soap of Marseille …") and complained that Prussia had to spend millions of thalers every year to buy these materials from abroad (Hermbstädt 1802).

Other useful sources that contain information about dyeing materials and techniques known in Prussia at that time


a)


b)


c)


d)

Figures 2 a–d: Typical examples of decorative silks from the New Palace, Potsdam Sanssouci (photos: W. Pfauder SPSG).
a) Damask dyed with cochineal (probably Berlin; around 1765)
b) Droguet from the dining room of the royal apartment dyed with mixtures of brazilwood, logwood and indigo (Jean-Baptiste Puis, Berlin; 1763–64)
c) Brocaded lampas from the "Jagdkammer" (hunting chamber) of the prince's upper chambers dyed with brazilwood and safflower (signature: "FBF a Berlin" = Brothers Baudouin and sons, Berlin; around 1765)
d) Brocaded lampas from the „Cammer coleur de Rose" (rose chamber) of the royal apartment dyed with safflower, weld and indigo (Girard and Michelet, Berlin; 1765).

are: "Werkstäte der heutigen Künste …" by Johann Samuel Halle (1727–1810), the "Oeconomische Encyklopädie" by Johann Georg Krünitz (1728–1796) and the "Technologisches Wörterbuch" as well as the "Schauplatz der Zeugmanufacturen in Deutschland" by Carl Gottfried Jacobsson (1725–1789) (Halle 1762, Halle 1765, Krünitz 1773–1858, Jacobsson 1773, Jacobsson 1781–1795). However, it should be mentioned that most recipes in these encyclopaedias originate from French writings.

3 Objects

The collection of the Prussian Palaces and Gardens Foundation contains a rich variety of plain coloured and brocaded silks. Some representative examples are shown in figure 2 a–d. All other objects are also pictured in the catalogue (Evers et al. 2014). More objects of the collection were analysed than are presented here. Only silks from the 18th century that are most likely of Prussian origin were selected for this paper.

The group of plain coloured silks mainly contains damasks and satins in red, blue, yellow and green. Twelve red, two yellow, and one green damask, one red velvet as well as one yellow and one blue satin of Prussian origin were analysed.

Eighteen fragments of brocaded silks from wall coverings of seven distinct pattern types were studied in detail, each containing several colours. Among them were brocaded satins, droguets and lampas.

4 Analytical methods

The textiles were studied with non- and micro-destructive methods. First, optical spectra were detected for each object. In most cases optical spectroscopy alone is not suitable for a certain identification of dyes. However, the method is non-destructive and fast. Therefore it was used as a preliminary test in order to identify groups of objects with comparable optical spectra. Objects from these groups were selected for further analysis. A CM-2600d Spectrophotometer (Minolta, Japan) equipped with pulsed xenon light sources, an integrating sphere, and a silicon photodiode array detector was used. The measurement spot size was 6 mm in diameter. Spectra were recorded in reflection mode in a range of 360 nm to 740 nm. They were compared to those of reference samples of silk dyed according to historical references.

An illumination with UV light (Reskolux UV365 lamp) was used as a preliminary test for safflower in the case of light red coloured silk. Safflower colours fluoresce in bright orange. A Chelsea filter was also helpful to distinguish between Prussian blue and indigo in the case of blue silk from the 18th century. Areas illuminated by light passing through the filter remain dark blue in the case of Prussian blue and are reddish in the case of indigo (Bartoll 2007).

Indigo was also identified non-destructively in green and blue silk using Raman spectroscopy (XploRA Raman microscope, Horiba Scientific, 785 nm laser excitation).

Thread samples of one to two centimetres length were taken from selected objects, when possible separately for warp and weft. In a first step, the threads were examined under the microscope. Thus mixed colours, colour changes, non-uniform dyeing as well as contaminations could be recognised.

In a second step, the threads were analysed using X-ray fluorescence spectroscopy (XRF). This method enables the identification of chemical elements such as aluminium, iron, cooper or tin. Their salts were often added as mordants in the dyeing process. XRF measurements were performed using the energy-dispersive micro X-ray fluorescence spectrometer "ARTAX" (Bruker AXS Microanalysis GmbH) equipped with a molybdenum tube and a helium purge. The spot size of the primary X-ray beam hitting the surface of the sample was in the range of 1.5 mm in diameter. All spectra were measured using a voltage of 45 kV and a current of 600 µA for the excitation.

The actual dyestuff analysis was performed using a High-Performance Liquid Chromatography system coupled with a photo diode array detector (HPLC-PAD). The dyestuff was removed from the fibres and dissolved as follows: about one milligram of silk sample (red, yellow, green or other mixed coloured fibres) was heated in 200 µl Dimethylformamide (DMF) for 10 minutes at 100 °C. After cooling down, the threads were removed, dried with filter paper, and heated again in 200 µl of a solution of two parts of concentrated hydrochloric acid (32%), one part of water and one part of methanol for ten minutes at 100 °C (Hofenk de Graaff 2004, Wouters & Verhecken 1989). Concentrated acetic acid was used instead of this solution in the case of a suspected brazilwood or safflower dye (e.g. as a result of the optical spectroscopy). Then the solution was decanted and dried in a desiccator over sodium hydroxide. The dried residue was dissolved in the DMF that was used in the first step. After centrifugation, 20 µl of the solution were injected into the HPLC system. Blue silks were only treated with DMF for ten minutes at 100 °C.

A "Smartline" analytical HPLC system (KNAUER, Germany) equipped with a PDA detector 2800 and analytical flow cell of 10 mm thickness was used. The HPLC column (KNAUER, 125 mm × 4 mm, Eurospher 100-5 C18) was tempered at 30 °C. Separation was achieved using the following elution program: 74A/16B/10C: two minutes; linear gradient to 0A/90B/10C: fifteen minutes; 0A/90B/10C: eight minutes; linear gradient to 74A/16B/10C: two minutes. The eluents consisted of (A) 10 vol% methanol in water; (B) methanol; (C) 0.5 wt% phosphoric acid in water. The flow rate was 0.6 ml / min.

5 Results

Table 1 summarises the dyeing materials most often mentioned in historical silk dyeing recipes. It also shows the dyestuff identified in the silk objects of the Prussian collection. The results will be presented in the following sections ordered by colours. Some information on the pre-treatment of silk will be outlined first.

5.1 Pre-treatment of silk

Before dyeing, the raw silk was boiled in soap water (von Pfeiffer 1780, Jacobsson 1773). Thereby the raw silk looses sericin proteins that glue the individual fibres together. This process is called degumming (Römpp Chemie Lexikon 1992). Thus the silk becomes softer, more flexible and shiny, but also lighter.

Usually, so-called Marseilles soap imported from France was used. According to Schmoller and Hintze, in 1771 there was only one manufacturer who was able to produce this soap in Berlin. His name was de Luna. In 1783 the Frenchmen de Serriere and Simon were granted the license to produce the soap in Berlin (Schmoller & Hintze 1892).

The historical sources often recommend a treatment of the degummed silk with metal salts (e.g. tin compounds) or tanning agents (e.g. gallnuts) in order to compensate for the lost weight. All silks studied here were analysed using XRF spectroscopy. The results show that the Prussian dyers in the 18th century did not use metal salts to weight the silk. The use of gallnuts was only observed here in the case of silk dyed with cochineal. Therefore the reason of its use was probably not to weight the silk (compare section "red colours").

So-called mordant dyes were usually applied. These dyes form a link with the silk proteins with the help of metal ions. Therefore the silk was treated with metal salt solutions ("mordants") usually before, but also during or after the actual dyeing process (Cardon 2007). Aluminium salt solutions (alum) were mainly used in this context, but also iron and tin salt solutions (Hofenk de Graaff 2004). The final colour of the silk was influenced by the kind of the metal ions used.

The results of this investigation show that all silk objects from the 18th century dyed with cochineal, weld or brazilwood were treated with alum. Occasionally iron and copper were also identified. Alum was probably obtained from Freienwalde on the river Oder. The alum plant in Freienwalde was owned by the Potsdam military orphanage (Ortloff 1798).

5.2 Blue colours

In 1802 Hermbstädt recommended woad, indigo and Prussian blue for the blue dyeing of wool, cotton and silk (Hermbstädt 1802). Other sources also mention indigo carmine (Saxon blue) and logwood (Haematoxylum campechianum L.) in this context.

Prussian blue was synthesised for the first time by Johann Jacob Diesbach in Berlin around 1706. The pigment was already used frequently at the Prussian court around 1710 (Bartoll & Jackisch 2010). It was also tested as a textile dye in France in the middle and in the second half of the 18th century (Anonymous, 1805). However, the results of this investigation show that the blue coloured silks of Prussian origin from the 18th century were not dyed with Prussian blue. The same is true for indigo carmine – a synthetic product of indigo and sulphuric acid – that has been used in textile dyeing from about the end of the 18th century (Hofenk de Graaff 2004).

Logwood is a native of the Yucatan peninsula and the neighbouring wetlands of Mexico (Hermbstädt 1802, Cardon 2007). Approximately 1800 logwood trees

Table 1: Comparison of dyeing materials mentioned in the historical sources (Hermbstädt 1802, Halle 1765, Jacobsson 1773) with those identified in the Prussian silk objects.

	Mostly recommended in the historical sources	*Identified in Prussian silk*
Blue shades	– indigo or woad (sometimes with addition of madder and orchil for priming) – Prussian blue – Saxon blue (indigo carmine)	– indigo or woad
Red shades	– cochineal – brazilwood (for darker shades with logwood; sometimes with annatto for priming) – safflower (sometimes with annatto for priming) – madder	– cochineal – brazilwood – safflower – mixtures of brazilwood, logwood and indigo
Violet shades	– cochineal + indigo – orchil (sometimes with indigo) – logwood – mixtures of logwood and brazilwood	– orchil – mixtures of orchil and indigo
Yellow shades	– weld – annatto (orange shades) – fustic – turmeric – young fustic – Persian berries – quercitron	– weld
Brown shades	– mixtures of brazilwood, logwood and fustic	– mixtures of logwood and weld
Green shades	– indigo + yellow (weld, sawwort, or dyer's broom, rarely: fustic, quercitron or turmeric), sometimes addition of logwood – indigo carmine + yellow	– indigo + weld – indigo + dyer's broom

were also cultivated on the Antilles (Hermbstädt 1802). Logwood is mostly recommended as an ingredient in recipes for mixed colours such as grey, brown, or violet shades. This was confirmed by the present analysis. Logwood was identified in red and brown shades, but not in pure blue silks of the Prussian collection (compare sections "red colours" and "yellow / brown colours").

Indigo was identified in the three blue silks of the 18th century analysed here by HPLC and Raman spectroscopy (figure 3). Its source could have either been woad (Isatis tinctoria L.) or indigo plants (various Indigofera species). A chemical differentiation of these sources analysing only the dyed textile fibres has not been possible so far (Hofenk de Graaff 2004).

In the 18th century woad was cultivated mainly in Thuringia. In 1802 Hermbstädt recommended the extension of the cultivation of woad in Prussia (Hermbstädt 1802). Frederick II himself supported the Prussian woad industry by founding an award for woad cultivation in 1772–74 (Rödenbeck 1838). However, David stated in his book on dyeing that woad did not play an important role in silk dyeing (David 1855).

In the second half of the 18th century most of the indigo used in Europe probably was derived from indigofera plants (Hofenk de Graaff 2004). They grow in many tropical and subtropical regions (Cardon 2007). In 1802 Hermbstädt reported that most of the indigo was imported from Santo Domingo to Prussia via Bordeaux, Le Havre, Nantes, Marseille, and Hamburg (Hermbstädt 1802). In 1784/85 Prussian merchant ships transported 5.718 pounds of Indigo from Asia to Prussia (Rödenbeck 1838).

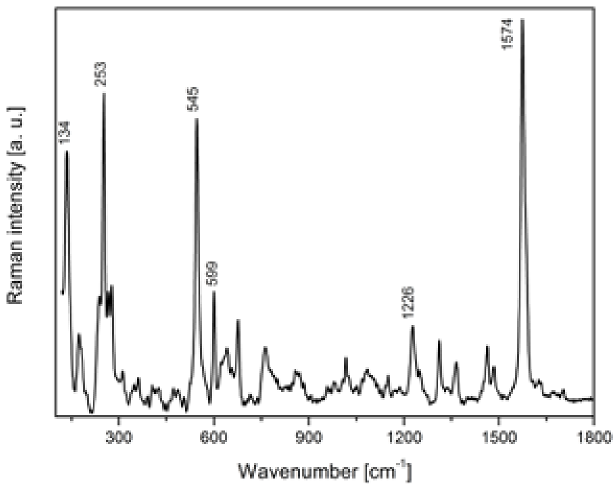


Figure 3: Raman spectrum of indigo on silk measured directly in the blue areas of the brocaded lampas from the „Cammer coleur de Rose" (compare figure 2d) using an excitation wavelength of 785 nm.

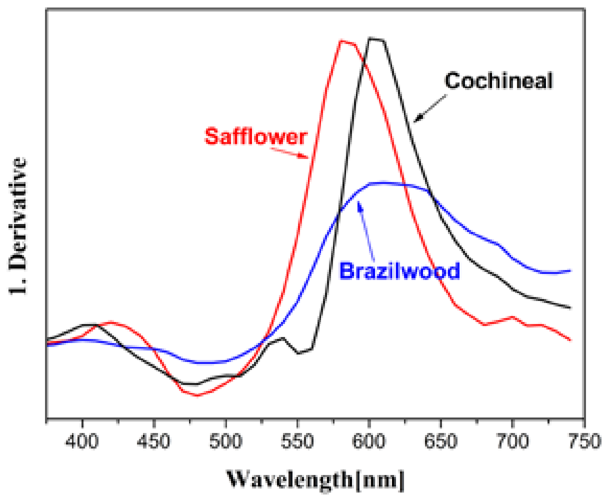


Figure 4: Typical optical reflection spectra (first derivative) of red silks of the Prussian collection. (Safflower and brazilwood: compare figure 2c; cochineal: red damask, inventory number: G.6 IX108, Girard and Michelet, Berlin; 1763).

5.3 Red colours

The historical sources of the 18th and the beginning of the 19th centuries mainly list cochineal, brazilwood and safflower as red dyestuffs for silk dyeing. Madder is also mentioned, even though it was mostly used for wool and cotton dyeing (Halle 1765, Vitalis 1824).

The optical reflection spectra of the red silk textiles studied here can be divided into three groups that differ in their spectral pattern (figure 4). The groups represent silk dyed with cochineal, brazilwood and safflower respectively, as was determined by further analysis using HPLC.

All red damasks from the 18th and the first half of the 19th centuries of the Prussian collection were dyed with cochineal (12 red damasks were analyzed; compare figure 2a). Various species of scale insects – such as kermes, cochineal, or Kerria lacca – produce anthraquinone dyes useful for silk dyeing (Caron 2007). In the 18th century the American cochineal (Dactylopius coccus Costa) from Mexico and South America dominated the European market. In earlier centuries a species from Central Europe (Porphyrophora polonica L. or Polish Cochineal or "Johannisblut") was used for dyeing too. However, already in 1736 Johann Leonhard Frisch – scholar in the field of silk production and colourants in Berlin – complained that the knowledge of the use of this local insect had been lost and that the cochineal had to be bought abroad (Frisch 1736). The composition of the colourants of the red silk analysed here (in general a low content of kermesic and flavokermesic acid in relation to the content of the main colourant carminic acid) also points to the use of American cochineal in Prussian silk dyeing of the 18th century (figure 5) (Wouters & Verhecken 1989, Serrano et al. 2011, Stathopolou et al. 2013).

Aluminium was detected with XRF analysis in all silk objects of the 18th century dyed with cochineal. Therefore, it is very likely that alum was used as a mordant. The use of tin or arsenic compounds as mentioned occasionally in the historical literature (von Pfeiffer 1780, Jacobsson 1773) can be excluded for the objects of the 18th century Prussian collection.

Ellagic acid was identified in all red damasks of the 18th century dyed with cochineal (figure 5). Its source is most likely gallnuts. In the second half of the 18th century gallnuts were imported from the eastern Mediterranean (the Levant). In 1765 Frederick II permitted the import from "Mussul, Smyrna and Aleppo" (Rödenbeck 1838).

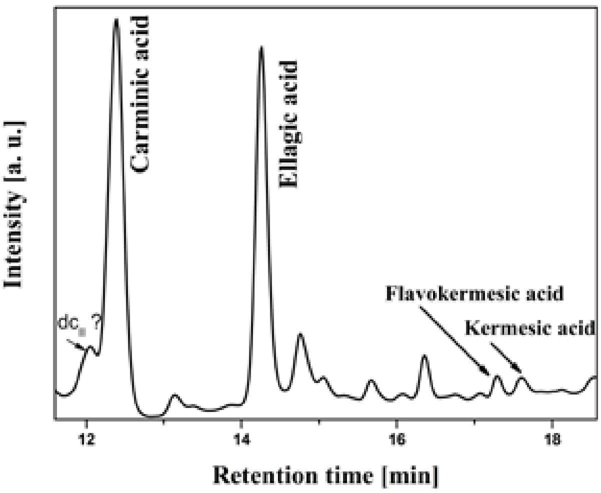


Figure 5: HPLC chromatogram (detected at 254 nm) of a red damask from the New Palace, Potsdam Sanssouci (probably Berlin, around 1765, inventory number: G.1E IX27).

The addition of gallnuts was part of many recipes in silk dyeing especially of those dealing with cochineal. The physical properties of silk can thus be altered, particularly adding weight. This effect was well known in the 18th century (Halle 1765). Dye factories that used gallnuts were therefore occasionally accused of being acquisitive (Hellot 1765). In 1766 Frederick II prohibited the use of gallnuts and other materials assigned to increase the weight of silk (Schmoller & Hintze 1892). Demonstrably, the Prussian dyers did not stick to this order in the case of the red damasks. The reason for this "offense" was probably not acquisitiveness – gallnuts were only used in the case of dyeing with cochineal – but rather due to dyeing techniques. The tanning agents of the gallnuts can influence the dyeing process in a positive way. For example, they can bind iron ions – which are always present for example in the water used – that might otherwise interfere with the dyeing process (Golikov 2001).

The use of gallnuts, which had thus already been discredited in the 18th century, decreased more and more during the 19th century. Therefore the damasks of the 19th century studied here, tend to contain less or no ellagic acid. This finding can be used to make a first assessment if red damask dates from the 18th or the 19th century. The dating of the decorative silks is an important task, because they were often renewed with the same pattern and technique due to their fragile nature.

After about 1860, cochineal was increasingly replaced by synthetic dyes. These substances can also be used for a relative dating (terminus post quem) of many objects, because in most cases, the date of their first production or product placement is known. For example, the synthetic dye Safranin was identified here in four cases in red wall coverings. The dye was patented in 1859 (Schultz & Julius 1897). Thus it could be proven that these silks were copies produced after 1859.

Brazilwood and safflower were used for the various shades of red in the brocaded fabrics (compare figure 2b – 2d; figure 6). Trees with soluble redwoods, the brazilwoods, grow in many parts of Asia (e.g. sappanwood) and America (e.g. pernambuco) (Cardon 2007). According to Jacobsson, brazilwood was imported to

Figure 6: Brocaded satin with chrysanthemum pattern from the bedrooms of the prince's chambers in the New Palace, Potsdam Sanssouci (Berlin; around 1765, inventory number: G.24 IX3418). Photo: W. Pfauder SPSG
Identified dyestuff: yellow: weld; red shades: mixtures of brazilwood, logwood, weld, indigo; brown: weld and logwood; green shades: mixture of indigo and weld (light green) or dyer's broom (dark green); violet: orchil and indigo.

a)

b)

Figures 7 a, b: Brocaded lampas from the "Jagdkammer" (hunting chamber) of the New Palace, Potsdam Sanssouci (Brothers Baudouin and sons, Berlin; around 1765; inventory number G.14A IX3628). The upper part of the silk was always covered from daylight, while the lower part was always exposed to it. Photos: W. Pfauder SPSG; **a)** visible light, **b)** UV light.

Europe from Brazil via Lisbon, England, and Holland in the 18th century (Jacobsseon 1773). Pernambuco wood had the best reputation. The Antilles and Japan were also sources for brazilwood. For example, in 1784/85 Prussian merchant ships of the "Asian company of Emden" brought 32.300 pounds of "Siapanholz" (Japan wood, brazilwood) from Asia to Prussia (Rödenbeck 1838). To date, it is hardly possible to analytically distinguish the various types of brazilwood species that were used for dyeing (Hofenk de Graaff 2004).

Brazilwood was always used with alum mordant in the textiles studied here. In some fabrics (for example figure 2b, figure 6) quite complex mixtures of brazilwood and other dyestuff yielded various colour shades from light pink to a dark reddish brown. An exquisite example is the wall covering with a chrysanthemum pattern from the New Palace, Potsdam Sanssouci (figure 6). The dark red shades were produced using a mixture of brazilwood, logwood and indigo. In addition, the lighter reds contain weld. Evidently, the Prussian silk dyers were experienced enough to handle quite complicated mixtures. Corresponding recipes can be found in the sources of the 18th century. For example, a famous colour named "Pompadour" was produced dyeing the silk with brazil- and logwood on a ground of weld (Cardon 2007).

The pink and orange shades in the brocaded lampas of the „Cammer coleur de Rose" (figure 2d) and the hunting chamber of the New Palace, Potsdam Sanssouci (figures 2c and 7a, b) were produced using safflower (Carthamus tinctorius L.). The distribution of safflower in a textile can be made visible under UV light illumination because of its bright orange fluorescence (figure 7b).

The annual spiny safflower plant has been cultivated in the eastern Mediterranean from earliest antiquity (Cardon 2007). The flower heads contain yellow and red colourants. Safflower is a direct dye used without mordant. According to Hermbstädt, safflower is an exquisite and indispensable red dyestuff in silk dyeing (Hermbstädt 1802). In 1772 and 1774 Frederick II awarded a prize for the cultivation of safflower in Prussia (Rödenbeck 1838). All the same, in 1802 Hermbstädt reported that there was still little effort in the cultivation of safflower in Prussia (Hermbstädt 1802). Therefore, most of the safflower had to be imported to Prussia from Egypt, the Levant, Indonesia or Thuringia (Hermbstädt 1802).

Both the main colourants of brazilwood and safflower, brazilein and carthamin respectively, have a poor light fastness. This effect can clearly be observed in the case of the wall covering of the hunting chamber (figure 7a, b). Areas always protected from daylight, for the most part show the original colours, whereas the colours in the areas always exposed to light, appear to have changed a lot over time. The light red shades (safflower) faded, the dark red areas (brazilwood) turned brown. The colour changes must have taken place quite early. In 1786 – not even 20 years after the mounting of the fabric – Nicolai described it as brown chenille (Nicolai 1786).

The light sensitivity of both dyes was well known in the 18th and 19th centuries (Halle 1765, Vitalis 1824). However, the dyers were most likely dependent on brazilwood and even more on safflower in order to create certain shades of red. The beautiful rose colour of the wall covering from the „Cammer coleur de Rose" of Frederick II in the New Palace, Potsdam is such an example. In this context Pfeiffer noted in 1780 that colours such as "ponceau, incarnate or cherry" cannot be created in silk using cochineal; safflower has to be used instead (von Pfeiffer 1780).

5.4 Violet colours

The recipes of the 18th century distinguish between genuine and false violet. According to Jacobsson the colour violet is either obtained using indigo and cochineal (genuine violet) or using orchil (false violet). Logwood and brazilwood were used too. A broad palette of violet and purple shades became available through mixing the ingredients mentioned above (Jacobsson 1773).

The fabric with chrysanthemum pattern (figure 6) is the only one in the collection with violet shades. As can be seen from the HPLC analysis (figure 8a, b) mixtures of orchil and indigo were used to produce these shades. No mordant was added.

Orchil is a dyestuff extracted from various lichen species belonging to the genera Roccella and Ochrolechia. The lichens grow, amongst others, on the rocks of the Mediterranean coasts, the Atlantic coasts of England, France and Portugal or in Scotland and Norway (Hofenk de Graaff 2004).

According to Pfeiffer the best orchil called "Kräuter Orseille" came from the Canaries around 1780 (von Pfeiffer 1780). In 1802 Hermbstädt mentioned an excellent orchil dyestuff manufactured in Italy (Hermbstädt 1802).

As in the case of brazilwood and safflower, orchil colourings are very light sensitive. This again was already known in the 18th century. Though in 1780 Pfeiffer praised the beauty of the orchil colour, he also complained about its bad durability. He stated that weak acids or the "bare air" cause this colour to fade and recommended keeping the dyed silk enclosed in order to preserve the colour (von Pfeiffer 1780).

5.5 Yellow / brown colours

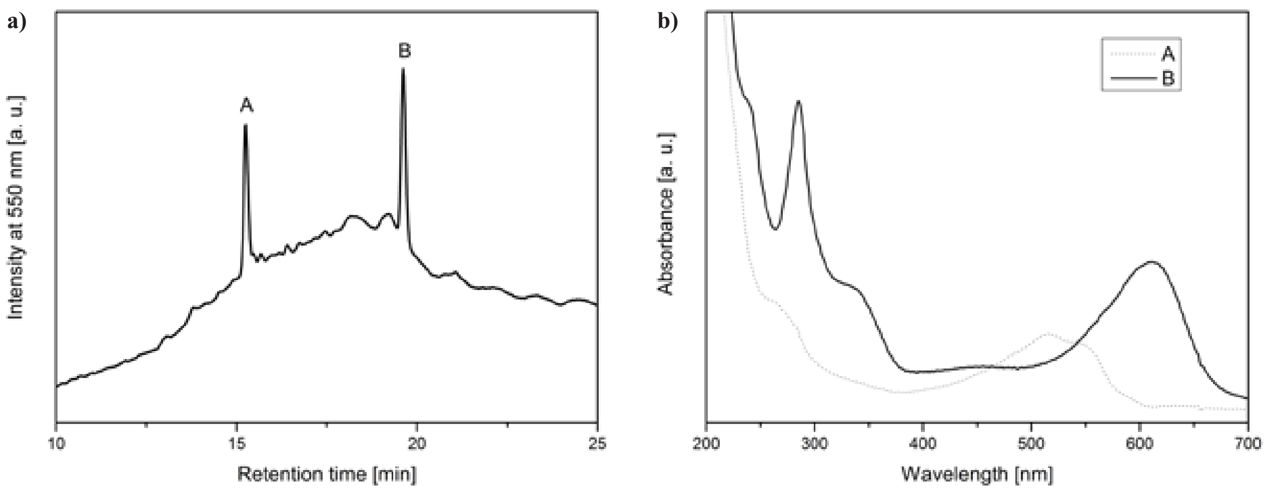
Weld (Reseda luteola L.) was mostly recommended for yellow silk dyeing in the historical sources of the 18th century (Jacobsson 1773). Furthermore, annatto (Bixa orellana L.), fustic (dyer's mulberry, Chlorophora tinctoria L.) and turmeric were mentioned in the context of orange shades or mixtures (Hermbstädt 1802, Halle 1765, Jacobsson 1773). Persian berries were less favoured because of the poor light fastness of their colour. Sawwort (Serratula tinctoria L.) and dyer's broom (Genista tinctoria L.) were mostly used together with indigo for greens (Halle 1765).

All yellow silk objects of the 18th century analysed here (three plain coloured silks, four brocaded silks as for example in figure 6) contain the flavones luteolin and apigenin. The dye plants weld, dyer's broom, and sawwort are likely to be possible sources of these compounds, bearing in mind region and time of use (Cardon 2007). Dyer's broom can easily be distinguished from the other two, because, in addition, it contains the isoflavone genistein or its glycosides respectively. It was not used for the yellow silk examined here.

The silks of this collection were most likely dyed with weld, even though the use of sawwort – especially in mixtures with weld – cannot be excluded definitely in many cases. Both dyestuffs only differ in minor compounds that are difficult to detect especially for aged samples and if – as usual – only small amounts of sample are available (Hofenk de Graaff 2004, Peggie et al. 2008, Lech et al. 2014).

Weld was already identified in French silk textiles of the 18th century (Ishii & Saito 2007). According to Hermbstädt weld originally came from France, but was also cultivated in other places such as in the state of Brandenburg (Hermbstädt 1802). Weld was therefore, among the few dyers' resources that did not have to be imported to Prussia. Alum was mostly used as a mordant for dyeing with weld. Aluminium was detected using XRF here in all samples dyed with weld.

Most recipes of the 18th century recommended mixtures of brazilwood, logwood, and yellow woods



Figures 8 a, b: HPLC analysis of the violet threads of the brocaded satin with chrysanthemum pattern (compare figure 6).
a) Chromatogram detected at 550 nm with two major peaks (A, B)
b) Optical absorption spectra corresponding to the peaks A (spectrum of an orcein, the main colouring matter of orchil) and B (spectrum of indigotin, the main colouring matter yielded from indigofera plants or woad).

for brown shades in silk (von Pfeiffer 1780, Halle 1765, Jacobsson 1773, David 1855). Mixtures of weld and gallnuts can also be found in this context (Hermbstädt 1830).

The brown shades in the fabric with the chrysanthemum pattern (figure 6) were composed using logwood and weld with an alum mordant. In the case of darker shades, iron salts were added.

5.6 Green colours

According to the handbook of silk dyeing from 1855, there was no important green dyestuff available. The green colour had to be created by mixing yellow and blue (David 1855). In a first step the silk was usually dyed with a yellow dye. That was typically weld, but Halle also recommended sawwort and dyer's broom as the yellow component in green dyeing (Halle 1765). In a second step the silk was dyed with indigo. In some cases logwood and yellow woods were also added depending on the shading one wanted to create (von Pfeiffer 1780, Halle 1765).

The green silk textiles from the 18th century studied here (one damask, two brocaded silks; compare figure 2d and figure 6) were dyed using indigo and a yellow dyestuff. For the damask and the lampas (figure 2d) this was weld. The green shades in the wall covering with the chrysanthemum pattern from the New Palace in Potsdam (figure 6) contain two yellow dyes. Weld was used for lighter greens, dyer's broom for darker colours. Again, this "fine tuning" of the shades through using different yellow components can be seen as evidence of the craftsmanship of the Prussian silk dyers.

6 Summary

The Prussian silk industry – including the silk dyeing – developed rapidly under the reign of Frederick II. Silk dyers from various European countries such as France, Italy, Holland or Switzerland were employed in Berlin and Potsdam. The immigrant dyers were supposed to pass their knowledge on to local craftsmen.

A large number of original silk textiles from the 18th century have been preserved in the collection of the Prussian Palaces and Gardens Foundation. For the first time this collection could also be studied in detail using scientific methods. Dyestuff analysis was performed on 36 objects. This offered a deep insight into the praxis of the Prussian silk dyeing of this period.

The Prussian palette of dyestuff corresponds largely with the written historical sources of the 18th century. This is especially true for the local works written by Hermbstädt, Halle and Jacobsson. The Prussian dyers did not use all materials mentioned in these books, but those that were found to be most suitable.

Cochineal, indigo and weld – all very suitable and relatively lightfast dyes for silk – were mostly used for plain red, blue, and yellow colours by the Prussian dyers. Alum was always used as a mordant for cochineal and weld. A mix of colour consisting of indigo and weld or dyer's broom was identified in green silk textiles. Brown shades were achieved through mixing weld and logwood. These mixtures were often "fine tuned" and quite complex and can be seen as a proof of the craftsmanship of the Prussian silk dyers. This also holds true for the red shades of the colourful patterned fabrics from rose, violet and orange to dark red.

However, for these red shades, "false" dyestuff sources – namely brazilwood, safflower and orchil – with poor light fastness were used by the dyers in otherwise high-quality fabrics. Today many objects in the Prussian collection dyed with these dyestuff sources appear brownish or faded. The problems concerning the light fastness of these dyes were known in the 18th century. Nevertheless, these materials – especially safflower but also brazilwood and orchil – were apparently indispensible in order to achieve certain shades of red that were particularly fashionable at that time.

Gallnuts were always added in dyeing the red damasks with cochineal in the 18th century. This was most likely done for reasons of dyeing techniques and not in order to weight the silk. This praxis vanished more and more in the 19th century. Therefore the extent of the use of gallnuts (or the relative concentration of ellagic acid in the HPLC analysis respectively) can be used as a rough dating tool for red damasks.

All the dyestuff used in Prussia – except the yellow dye plants – most likely had to be imported from abroad. Many materials came from far away regions in Asia or Middle and South America. This means that even though Frederick II had succeeded in establishing a powerful silk industry in Prussia, he could not completely fulfil his aim of becoming independent from expensive imports.

7 Acknowledgements

The author is grateful to Susanne Evers, Christa Zitzmann and the colleagues of the department of textile conservation (SPSG) for a pleasant and fruitful cooperation. The author also wishes to thank Christine Fuchs and Steffen Laue (University of Applied Sciences, Potsdam) for stimulating discussions and technical support.

References

Anonymous (1805): *Von dem Berlinerblau, dessen Gebrauch bei der Färberei, und von einer neuen aus dieser Substanz gewonnenen Farbe.* In: Magazin der Handels- und Gewerbekunde vol. 3, iss. 2, 437 – 458

Bartoll, J., Jackisch, B. (2010): *Prussian Blue – A Chronology of the Early Years.* In: Zeitschrift für Kunsttechnologie und Konservierung 24, iss 1, 88 – 102

Bartoll, J. (2007): *Dichromatische Farbfilter – Ein Hilfsmittel bei der Pigmentanalyse und Restaurierung.* In: Restauro, iss 3, 178 – 181

Cardon, D. (2007): *Natural Dyes: Sources, Tradition, Technology and Science* (Archetype Publications) London, p. 14, 54, 169 – 181, 264, 274 – 289, 285, 353, 607 – 666

David, P. (1855): *Vollständiges Handbuch der Seidenfärberei, theoretisch und insbesondere practisch zum Gebrauch für Färber und Fabrikanten bearbeitet von Philipp David, gelernter Seidenfärber aus Basel* (H. R. Sauerländer) Aarau, p. 114, 145, 177

Evers, S. (2014): Seidenkunst im Spiegel der Raumausstattungen Friedrichs II. in Berlin und Potsdam, in: Evers S., Zitzmann C., Kuschel, N., Kreibich, S., Bartoll, J.: *Seiden in den preußischen Schlössern. Ausstattungstextilien und Posamente unter Friedrich II. (1740 – 1786). Mit Beiträgen von Petra Raschkewitz und Friederike Wappenschmidt,* (de Gruyter) Berlin, 3 – 54

Evers S., Zitzmann C., Kuschel, N., Kreibich, S., Bartoll, J. (2014): *Seiden in den preußischen Schlössern. Ausstattungstextilien und Posamente unter Friedrich II. (1740 – 1786). Mit Beiträgen von Petra Raschkewitz und Friederike Wappenschmidt*, (de Gruyter) Berlin

Fidicin, E. (1858): *Die Territorien der Mark Brandenburg, Theil II, Die Stadt und Insel Potsdam*, (Verlag von J. Guttentag) Berlin, 134 – 135

Frisch, J. L. (1736): *Beschreibung von allerley Insecten in Teutschland, vol 5*, (Nicolai) Berlin, 10

Golikov, V. (2001): *The Technology of Silk Dyeing by Cochineal. III. The Experimental Investigation of the Influences of pH, Water Quality, Cream of Tartar and Oak Galls.* In: Dyes in History and Archaeology 16/17, 21 – 33

Halle, J. S. (1762): *Werkstäte der heutigen Künste, oder die neue Kunsthistorie, vol. 2.* (Johann Wendelin Halle und Johann Samuel Halle) Brandenburg and Leipzig, 216, 385 – 387

Halle, J. S. (1765): *Werkstäte der heutigen Künste, oder die neue Kunsthistorie. vol. 4,* (Johann Wendelin Halle und Johann Samuel Halle) Brandenburg and Leipzig, 273 – 292

Hellot, J. (1765): *Des Herrn Hellots Färbekunst oder Unterricht Wolle und wollene Zeuge zu färben, zweyte Auflage, welcher eine Nachricht von der Seidenfärberey beygefügt ist,* (Richterische Buchhandlung) Altenburg, 376

Hermbstädt, S. F. (1802): *Grundriß der Färbekunst oder allgemeine theoretische und praktische Anleitung zur rationellen Ausübung der Wollen-, Seiden-, Baumwollen- und Leinenfärberey; so wie der damit in Verbindung stehenden Kunst, Zeuge zu drucken und zu bleichen: nach physikalisch-chemischen Grundsätzen und als Leitfaden zu dem Unterrichte der inländischen Färber, Zeugdrucker und Bleicher auf allerhöchsten Befehl entworfen,* (Nicolai) Berlin and Stettin, p. 31, 352, 363 – 364, 376 – 377, 382, 384, 397, 512, 566, 873

Hermbstädt, S. F. (1830): *Grundriß der Technologie; oder Anleitung zur rationellen Kenntniß und Beurtheilung derjenigen Künste, Fabriken, Manufakturen und Handwerke, welche mit der Kameral= und Policeywissenschaft, so wie der Landwirthschaft in nächster Verbindung stehen,* (G. Reimer) Berlin, 316

Hofenk de Graaff, J. H. (2004): *The Colourful Past – Origins, Chemistry and Identification of Natural Dyestuffs,* (Abegg-Stiftung and Archetype Publications), p. 11, 16, 35 – 41, 147, 214, 240, 257, 259, 275

Ishii, M., Saito, M. (2007): *HPLC analysis of natural yellow dyes in 18th century French silk textiles.* In: Bunkazai hozon-syuhuku gakkaisi 52, 37 – 52

Jacobsson, J. K. G. (1773): *Schauplatz der Zeugmanufacturen in Deutschland – Beschreibung aller Leinen= Baumwollen= Wollen= und Seiden = Arbeiten, wie sie in den Königlich=Preußischen und Churfürstlich=Brandenburgischen Landen verfertigt werden, vol. 1,* (August Mylius) Berlin, 305 – 306, 486 – 554

Jacobsson, J. K. G. (1781 – 1795): *Technologisches Wörterbuch, alphabetische Erklärung aller nützlichen mechanischen Künste, Manufakturen, Fabriken und Handwerker*, (Nicolai) Berlin and Stettin

Krünitz, J. G. (1773 – 1858): *Oekonomische Encyclopädie oder allgemeines System der Staats-, Stadt-, Haus- und Landwirthschaft in alphabetischer Ordnung.* 242 volumes, Berlin

Lech, K., Witkoś, K., Jarosz, M. (2014): *HPLC–UV–ESI MS/MS identification of the color constituents of sawwort (Serratula tinctoria L.).* In: Anal Bioanal Chem, 3703 – 3708

Martin, W. (1989): *Manufakturen im Berliner Raum seit dem ausgehenden 17. Jahrhundert,* (Gebr. Mann Verlag) Berlin, 169 – 173

Nicolai, Ch. F. (1769): *Beschreibung der Königlichen Residenzstädte Berlin und Potsdam und aller daselbst befindlicher Merkwürdigkeiten,* (Friedrich Nicolai) Berlin, 309 – 310

Nicolai, Ch. F. (1786): *Beschreibung der Königlichen Residenzstädte Berlin und Potsdam, aller daselbst befindlicher Merkwürdigkeiten und der umliegenden Gegend, third edition,* (Friedrich Nicolai) Berlin, 514, 1242

Ortloff, J. A. (1798): *Handbuch einer allgemeinen Statistik der Königlich Preußischen Staaten. Erste Abteilung,* (Walthersche Buchhandlung) Erlangen, 55 – 56

Peggie, D. A., Hulme, A. N., McNab, H., Quye, A. (2008): *Towards the identification of characteristic minor components from textiles dyed with weld (Reseda luteola L.) and those dyed with Mexican cochineal (Dactylopius coccus Costa).* In: Microchimica Acta 162, 371 – 380

Pfeiffer, J. F. von (1780): *Die Manufacturen und Fabricken Deutschlands nach ihrer heutigen Lage betrachtet und mit allgemeinen Vorschlägen zu ihren vorzüglichsten VerbesserungsMitteln begleitet, vol. 1,* (Barrentrapp Sohn und Wennet) Frankfurt am Main, 341 – 375, 372 – 375

Rödenbeck, K. H. S. (1838): *Finanzsystem Friedrichs des Großen in Bezug auf Fabrikwesen, Handel und Landwirtschaft,* (Verlag der Plahnschen Buchhandlung) Berlin, p. 216 – 217, 327, 405, 406

Römpp Chemie Lexikon (1992), vol. 5, ninth edition (Georg Thieme Verlag) Stuttgart, 4095

Schmoller, G., Hintze, O. (1892): *Die Preußische Seidenindustrie im 18. Jahrhundert und ihre Begründung durch Friedrich den Großen, vol. 1,* (Verlag von Paul Parey) Berlin, p. 35, 75 – 76, 298, 401, 434, 481

Schultz, G., Julius, P. (1897): *Tabellarische Übersicht der im Handel befindlichen künstlichen organischen Farbstoffe,* (Gaertners Verlagsbuchhandlung) Berlin, 183

Serrano, A., Sousa, M. M., Hallett, J., Lopes, J. A., Oliveira, M. C. (2011): *Analysis of natural red dyes (cochineal) in textiles of historical importance using HPLC and multivariate data analysis.* In: Anal Bioanal Chem 401, 735 – 743

Stathopoulou, K., Valianou, L., Skaltsounis, A-L., Karapanagiotis, I., Magiatis, P. (2013): *Structure elucidation and chromatographic identification of anthraquinone components of cochineal (Dactylopius coccus) detected in historical objects.* In: Analytica chimica acta 804, 264 – 272

Vitalis, J. B. (1824): *Lehrbuch der gesammten Färberei auf Wolle, Seide, Leinen, Hanf und Baumwolle,* (Bernh. Fr. Voigt) Ilmenau, 168, 222

Wouters, J., Verhecken, A. (1989): *The coccid insect dyes: HPLC and computerized diode-array analysis of dyed yarns.* In: Studies in Conservation 34, 189 – 200

Wouters, J., Verhecken, A. (1989): *The Scale Insect Dyes (Homoptera: Coccoidea). Species Recognition by HPLC and Diode-Array Analysis of the Dyestuffs.* In: Annls Soc. ent. Fr. (N.S.) 25, 393 – 410

Corresponding author:
Jens Bartoll (j.bartoll@spsg.de)