



## Hexacyanoferrate: Approach for pigment analysis, early extraction, production, properties and uses

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### Abstract

The cobalt hexacyanoferrate-decorated titania nanotube (CoHCF@TNT) was prepared by dispersing 100 mg of titania nanotube (TNT) to a solution of an equimolar concentration of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  containing 0.05M KCl solution (35mL). The TNT was synthesized by hydrothermal method using Degussa P-25  $\text{TiO}_2$  in 2M NaOH as reported in the literature. As far as is known, the pigment Prussian blue was synthesised for the first time in Berlin in the early 1700s. It is commonly assumed that the pigment was not used in paintings before the 1720s. The presence or absence of this pigment is often used to answer questions concerning the dating and authenticity of art objects from the 18th Century. For the very first time, a large collection of French 18th Century paintings by Antoine Watteau (1684-1721) and his circle has been studied in detail. The pigments of more than fifty paintings from the collection of Frederick II of Prussia have been analysed with non-destructive methods using a complementary combination of micro X-ray fluorescence analysis, optical microscopy and spectroscopy in reflection mode.

Most interesting in this context is evidence of Prussian blue in two earlier works by Watteau from about 1710. It shows that Prussian blue must have found its way from Berlin to Paris by around 1710 at the latest. In the search for further proof that Prussian blue was used in paintings dating back to the same years, we also analysed blue pigments in works by painters of the Prussian court, and of other European courts. The court painters were closely connected to the Royal Academy of Arts in Berlin, where the pigment was available no later than 1709. This investigation shows that Prussian blue was used by painters at the Prussian court, in Rotterdam, and Paris much earlier than previously assumed. It was already used in 1710, and this to a surprisingly large extent. To date, the painting "Entombment of Christ", dated 1709 by Pieter van der Werff (Picture Gallery, Sanssouci, Potsdam) is the oldest known painting where Prussian blue has been used. Historical sources and the material findings mentioned above date the first synthesis of the pigment by Johann Jacob Diesbach in Berlin to about 1706.

**Keywords:** pigments, paintings, method, oxidation, material findings

### Introduction

Prussian blue is a dark blue pigment with the idealized formula  $\text{Fe}_7(\text{CN})_{18}$ . Another name for the color Prussian blue is Berlin blue or, in painting, Parisian blue. Turnbull's blue is the same substance but is made from different reagents. Prussian blue was one of the first synthetic pigments. It is employed as a very fine colloidal dispersion, as the compound itself is not soluble in water. It is famously complex, owing to the presence of variable amounts of other ions and the sensitive dependence of its appearance on the size of the colloidal particles formed when it is made. The pigment is used in paints, and it is the traditional "blue" in blueprints.

The Prussian Palaces and Gardens Foundation Berlin-Brandenburg in Potsdam, Germany, is presently preparing a catalogue of its collection of French 18th-century paintings collected by Frederick II of Prussia (1712-1786) [catalogue]. Works by Antoine Watteau (1684-1721), Nicolas Lancret (1690-1743), and Jean-Baptiste Pater (1695-1736) feature prominently in this collection. A team of art historians, restorers and scientists is currently investigating more than 50 paintings. For the first time, one of the largest collections of its kind is being studied in-depth.

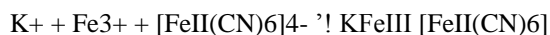
This study shows that the pigment Prussian blue, an iron hexacyanoferrate complex compound, was used by the painters in Paris much earlier than has been previously

assumed [Bartoll *et al.*]. Most surprising was the evidence of Prussian blue in two earlier paintings by Watteau: "La mariée de village" (SPSG, Potsdam, Sanssouci Palace, see Figure 1) and "Embarkation to Cythera" (Städel Museum, Frankfurt). Both paintings are conventionally dated to around 1710.

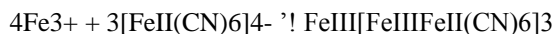
### Production

Prussian blue is produced by oxidation of ferrous ferrocyanide salts. These white solids have the formula  $\text{M}_2\text{Fe}[\text{Fe}(\text{CN})_6]$  where  $\text{M}^+ = \text{Na}^+$  or  $\text{K}^+$ . The iron in this material is all ferrous, hence the absence of deep color associated with the mixed valency. Oxidation of this white solid with hydrogen peroxide or sodium chlorate produces ferricyanide and affords Prussian Blue.

A "soluble" form of PB,  $\text{K}[\text{FeIII}(\text{CN})_6]$ , which is really colloidal, can be made from potassium ferrocyanide and iron(III):



The similar reaction of potassium ferricyanide and iron (II) results in the same colloidal solution, because  $[\text{FeIII}(\text{CN})_6]^{3-}$  is converted into ferrocyanide. "Insoluble" Prussian blue is produced if in the reactions above an excess of  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ , respectively, is added. In the first case:



One of the best examples of serendipity turned to advantage is the history of the coloring material Prussian blue. Accounts of its invention and subsequent development were familiar to readers of all interests, discussed along with descriptions of the process. Prussian blue including its history—was both an intellectual and a practical model for several color making practices at the time.

The story proved the close relationship between sciences and practices, and highlighted the opportunities each could provide the other.

Le rouge de Prusse est une substance donnant un rouge imitant le vermillon, qui sert communément aux Peintres d'impression, à mettre les carreaux en rouge, & aux Peintres à talens, pour leurs tableaux. Il est plus beau, plus vif que le brunrouge d'Angleterre: Selon les uns, c'est une terre calcinée; selon d'autres, dont je crois l'opinion fondée, c'est le colcothar ou caput mortuum des eaux fortes qu'on réduit en poudre fine, après avoir bien lavées.

Jean-Félix Watin, *L'Art du peintre, doreur, vernisseur* 4th ed. (Paris, 1787), 22–23. Eighteenth-century descriptions and discussions give the impression of considerable interest in the chemical foundations of Prussian blue—how it was created and how to use that information to make the color less expensive, more predictable, less likely to turn green with time, easier to work. Other investigators explored its possibilities as a key to chemical combination for other painters' pigments. In the 1790s, Thomas Henry read a letter to the Manchester Literary and Philosophical Society, announcing the discovery of some colors similar to Prussian blue. Henry's chemical analysis of those new colors employed contemporary chemical language and techniques, but his description of the processes of discovery more closely resembles the story recounted by Stahl sixty years earlier.<sup>7</sup> Other "Prussian" colors appeared, some involving production processes similar to that of Prussian blue, others merely relying on this designation to suggest a connection to this familiar and successful scientific novelty.

### Approach of pigment analysis

The search for Prussian blue in paintings of the beginning of the 18<sup>th</sup> Century can be rather difficult. This holds especially true for Watteau, as many of his paintings have undergone several conservation and restoration campaigns, often dating back to as early as the 18<sup>th</sup> Century. This makes not only the analysis of pigments difficult; there is also the risk of confusing original with later ingredients. The Prussian blue applied by the artists reacts sensitively to light. In some paintings it has strongly faded, or has changed into a grey colour.

A basic principle of this investigation was to take no samples from the visible areas of the paintings. The pigments were studied with non-destructive methods, using a complementary combination of optical microscopy, micro X-ray fluorescence analysis and optical spectroscopy in reflection mode [Bartoll *et al.*].

In a few cases, samples were taken from paint layers from the outer edges or tacking margins of the painting, in order to produce cross sections, and to carry out infrared spectroscopy.

The X-ray fluorescence (XRF) measurements were performed using the mobile energy dispersive X-ray fluorescence spectrometer "ARTAX" (Bruker AXS Microanalysis GmbH, Berlin, Germany) [Bronk *et al.*]. The use of open helium purging equipment for the excitation and detection paths enabled the detection of all elements down to sodium. All spectra were measured using a voltage of 45 kV, and a current of 600  $\mu$ A for the excitation.

The shape and size of the pigment grains were observed directly on the paintings using an optical microscope (Carl Zeiss OPMI1-FC; magnification up to 50x). Ultramarine appears in rather large particles through the optical microscope.

Prussian blue and indigo are fine powders (grain size < 1  $\mu$ m). Thus, when observing the surface of the painting through the microscope, only a blue coloured matrix should ideally be visible for the latter two pigments. The powder particles, however, often stick together and for this reason, they cannot always be distinguished from mineral pigments with certainty using this method.

Thus, a third non-destructive method was applied: optical spectroscopy in reflection mode [Johnston-Feller]. This was performed using a CM-2600d Spectrophotometer (Minolta, Japan) equipped with pulsed xenon light sources, an integrating sphere, and a silicon photodiode array detector. The measurement spot size was 3 mm in diameter. Spectra were recorded in reflection mode at a range of 360 nm to 740 nm, with a step size of 10 nm. They were compared to those of positively identified pigments in original paintings. It shows optical reflection spectra of blue pigments measured directly on the original paintings. As can be seen, the spectra differ significantly. The spectra of ultramarine and indigo show a strong reflection in the red range above 650 nm. Prussian blue does not have this red component.

### Properties

Prussian blue is a microcrystalline blue powder. It is insoluble, but the crystallites tend to form a colloid. Such colloids can pass through fine filters.

Despite being one of the oldest known synthetic compounds, the composition of Prussian blue remained uncertain for many years. The precise identification of Prussian blue was complicated by three factors:

1. Prussian blue is extremely insoluble but also tends to form colloids;
2. Traditional syntheses tend to afford impure compositions;
3. Even pure Prussian blue is structurally complex, defying routine crystallographic analysis.

### Crystal Structure

The chemical formula of insoluble Prussian blue is  $\text{Fe}_7(\text{CN})_{18} \cdot x\text{H}_2\text{O}$ , where  $x = 14\text{--}16$ . The structure was determined by using IR spectroscopy, Moessbauer spectroscopy, X-ray crystallography, and neutron crystallography. Since X-ray diffraction cannot distinguish carbon from nitrogen, the location of these lighter elements is deduced by spectroscopic means as well as by observing the distances from the iron atom centers.

PB has a cubic lattice structure. Soluble PB crystals contain interstitial  $\text{K}^+$  ions; insoluble PB has interstitial water instead.

In ideal insoluble PB crystals, the cubic framework is built from Fe(II)-C-N-Fe(III) sequences, with Fe(II)-carbon distances of 1.92 Å and Fe(III)-nitrogen distances of 2.03 Å. One-fourth of the sites of Fe(CN)<sub>6</sub> subunits are vacant (empty), leaving three such groups. The empty nitrogen sites are filled with water molecules instead, which are coordinated to Fe(III).

### Color

Prussian blue is strongly colored and tends towards black and dark blue when mixed into oil paints. The exact hue depends on the method of preparation, which dictates the particle size. The intense blue color of Prussian blue is associated with the energy of the transfer of electrons from Fe(II) to Fe(III). Many such mixed valence compounds absorb certain wavelengths of visible light resulting from intervalence charge transfer. In this case, orange-red light around 680 nanometers in wavelength is absorbed, and the reflected light appears blue as a result.

Like most high chroma pigments, Prussian blue cannot be accurately displayed on a computer display, but this swatch gives a common approximation, the sRGB colour #003153, intended for viewing on an output device with a gamma of 2.2.

PB is electro chromic—changing from blue to colorless upon reduction. This change is caused by reduction of the Fe (III) to Fe (II) eliminating the inter valence charge transfer that causes Prussian blue's color.

### Early Prussian Blue- Material Findings

Watteau, Adrian van der Werff (1659-1722), and Giovanni Antonio Canal (Canaletto) (1697- 1768), are frequently mentioned in literature as the first painters to have used Prussian blue in easel painting [Berrie]. However, the earliest works by Canaletto containing Prussian blue date back to the time between 1719 and 1723, which is rather late in this context. More recently, evidence of Prussian blue was found in paintings by the Austrian artists Jacopo Zanussi, Johann Georg Schmidts, and Franz von Tamm from 1715 [Richard *et al.*]. The pigment was also found in a painting by the Dutch painter Matthys Naiveau again from 1715 [Groen].

Traces of Prussian blue may be present on the decorated fencing from 1712/13 at Charlottenburg Palace, Berlin [Becker]. The investigations presented here concentrate on Paris (Watteau and his circle), Düsseldorf / Rotterdam (van der Werff brothers), and, last but not least, on Prussia as the place of origin.

### Paris: Pater, Lancret, Watteau

The paintings by Pater of the Prussian collection date back to around 1728 to 1736 [catalogue]. Prussian blue was the only blue pigment detected in all twenty-five paintings investigated here [Bartoll *et al.*]. Even green colours are all a mix of Prussian blue and Naples yellow.

Thirteen of the eighteen paintings by Lancret investigated here contain Prussian blue. Lancret produced these works between about 1719 and 1743 [catalogue]. In his earlier works, he still used more ultramarine, whereas his later works are increasingly dominated by Prussian blue.

Most typical of this artist is his use of ultramarine for the sky and Prussian blue for the figures. He used mixed greens with

Prussian blue in addition to green earth pigments [Bartoll *et al.*]. It is assumed that Prussian blue was used in the painting “Comédiens italiens”, National Gallery of Art, Washington (D. C.) [Fisher].

However, the painting might only be a copy after Watteau [Börsch-Supan 2000]. The thirteen paintings by Watteau investigated here date back to about 1709 to 1721. Prussian blue was identified in five of them [catalogue]. These are: “Recréation italienne” (Sanssouci Palace, Potsdam; see also [Becker]), “La mariée de village” (Sanssouci Palace, Potsdam), as well as the Italian and the French comedies (both Gemäldegalerie Berlin, SPK). His work, the “Embarkation to Cythera”, today in the Städel Museum, Frankfurt, Germany, also very likely contains the pigment (optical spectroscopy and microscopy SPSG; REM-EDX by M. Eveno, C2RMF, Louvre, Paris). Watteau used Prussian blue in these paintings in combination with ultramarine. Greens mixed with Prussian blue were not identified in the case of Watteau.

### Uses

#### Pigment

Because it is easily made, cheap, non-toxic, and intensely colored, Prussian blue has attracted many applications. The dominant uses are for pigments: approximately 12,000 tonnes of Prussian blue are produced annually for use in black and bluish inks. A variety of other pigments also contain the material. Engineer's blue and the pigment formed on cyanotypes—giving them their common name blueprints. Certain crayons were once colored with Prussian blue (later relabeled Midnight Blue). It is also a popular pigment in paints. Similarly, Prussian blue is the basis for laundry bluing.

#### Medicine

Prussian blue's ability to incorporate monocations makes it useful as a sequestering agent for certain heavy metal poisons. Pharmaceutical-grade Prussian blue in particular is used for patients who have ingested thallium or radioactive caesium. According to the International Atomic Energy Agency, an adult male can eat at least 10 grams of Prussian blue per day without serious harm. The U.S.

Food and Drug Administration (FDA) has determined that the “500 mg Prussian blue capsules, when manufactured under the conditions of an approved New Drug Application (NDA), can be found safe and effective therapy” in certain poisoning cases. Radiogardase (Prussian blue in soluble capsules) is a commercial product for the removal of caesium-137 from the intestine and so indirectly from the bloodstream by intervening in the enterohepatic circulation of caesium-137, reducing the internal residency time (and exposure) by about two-thirds.

#### Analytical Chemistry

Prussian blue is formed in the Prussian blue assay for total phenols. Samples and phenolic standards are given acidic ferric chloride and ferricyanide which is reduced to ferrocyanide by the phenols. The ferric chloride and ferrocyanide react to form Prussian blue. Comparing the absorbance at 700 nm of the samples to the standards allows for the determination of total phenols.

## Conclusion

Prussian blue was probably synthesised for the first time by Johann Jacob Diesbach in Berlin around the year 1706. Shortly after, not later than 1708, Johann Leonhard Frisch began to promote and sell the pigment across Europe. The pigment was first named "Preussisch Blau", and later, in November 1709, the name was changed to "Berlinisch Blau". The pigment was accepted by artists much earlier than previously assumed, as can be proven on the basis of a number of examples.

To date, the painting "Entombment of Christ" (Picture Gallery, Sanssouci, Potsdam, dated 1709) by Pieter van der Werff is the oldest known painting that makes use of Prussian blue. Around 1710, painters at the Prussian court such as Pesne, Gericke, Manyóki, and Weidemann were already using the pigment to a surprisingly large extent. At around the same time, Prussian blue arrived in Paris, where Watteau and later his successors Lancret and Pater used it in their paintings.

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