ON TWO LETTERS FROM CASPAR NEUMANN TO JOHN WOODWARD REVEALING THE SECRET METHOD FOR PREPARATION OF PRUSSIAN BLUE

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Introduction

Prussian Blue (ferric hexacyanoferrate(II)) was discovered accidentally by Johann Jacob Diesbach (1) and Johann Konrad Dippel (2) in Berlin in 1706 (3). As the first synthetic pigment, Prussian Blue received its name from the country in which its discovery occurred. It revolutionized the use of the color blue in artwork because it was less expensive and/or more stable than other blue pigments of the time.

In February, 1707, soon after the discovery of the Prussian Blue, Dippel fled Berlin to the Netherlands to avoid a second imprisonment (3). In the following years, Prussian Blue was produced and marketed by Diesbach and Johann Leonhard Frisch (4) in Berlin (3), at least until 1716, and for a certain time also by Dippel in the Netherlands (3). Next to nothing is known about Dippel's Prussian Blue production in the Netherlands prior to his departure from that country in 1714. The Prussian Blue manufacture in Berlin, on the other hand, was a great commercial success (3). Throughout Europe, people were interested in the secret to its production; but for obvious reasons, the manufacturers tried to protect their process. Frisch reported to Leibniz in a letter dated October 29, 1712 that some Italians wanted to buy the secret of the Prussian Blue production (5), but their offer was too low to match the high profits he realized with the production monopoly. Suddenly, in 1724, John Woodward (6), from London published a detailed description of the preparation process for Prussian Blue in the *Transactions of the Royal Society* (7). This production method had been sent to him from Germany. Until recently, the identity of the sender has been unknown, but this information is to be found in the archives of the Royal Society in London.

The Two Letters from Caspar Neumann to John Woodward

In the archives of the Royal Society, the excerpts of two communications from Caspar Neumann in Germany to John Woodward from the year 1723 can be found (8, 9). In the excerpt of the first letter, written in English in June, 1723, the following writing of Neumann to John Woodward is recorded (8):

I am Still A Debtor to the Royal Society, to recommend my Self to them by Something or other that may be curious or usefull. For which reason I have been continually hitherto thinking on some way or other of discharging my Obligation in that Respect; but still nothing presented itself for my said Purpose. however now I have thought on a certain blew die of as deep a Colour as that of the flower Gentianella is. It is a Product of Alum and Sal Alkali precipitated by certain Knacks or manual Operations. Painters may use it with great advantage instead of Ultramarine. The first Inventor of it lives in Berlin: his name is Mr. Frisch, Conrector of the school of that Town, who is the onely Man that prepares it, and Sells a great quantity of it for Italy, and Germany, and I don't know but for England too.

This Arcanum I should be willing to communicate to the Royal Society, provided it might prove acceptable to them: for else, if they should not value it, I should be loath to divulge it, and so make this pretty art known to the world, and thereby deprive that Gentleman of the Advantage and profit he draws from it, he being a good friend of mine. Indeed he never taught it me, nor did I ever exchange one word or Letter with him about it; but whatever Inkling or hint I had concerning some of the Ingredients, I by my Self found out the preparation thereof, by many Trials, and by my own Industry, with great cost and charges; So that I am able to prepare the Colour bright, dark, violet or purple, and yet all these of one and the same Stuff, the manual Operations do differ, and therein chiefly the Art consists. Yet I am not willing to communicate it under mine own Name, but Shall be content, if somebody else be said to be the Communicator of it. Wherefore if this Secret be not already known in England, I intreat you to acquaint me by your next, if the Communication thereof would prove acceptable or no, and then the Process, with all the several manuals, Shall be imparted, as soon as possible, by the Post.

Obviously, Woodward wrote back to Neumann that his information on the Prussian Blue manufacture would be



Figure 1. Caspar Neumann, apothecary and chemist from Berlin, who revealed the heretofore secret production method of Prussian Blue to John Woodward in 1723 (© Leopoldina, Halle, Germany).

welcome for the Royal Society because the above extract of the first Neumann letter is followed in the Register Book of the Royal Society by the production method for Prussian Blue sent by Neumann and dated 'Lips. 17. Nov. 1723,' written in Latin (9). Interestingly, both Neumann texts were sent or at least are shown to be sent from 'Lipsick' or 'Lips.,' i.e., Leipzig, a city in the German state Saxony about 150 km south of Berlin. Perhaps Neumann chose Leipzig to conceal that the sender of the Prussian Blue production method was located in Berlin.

From the extract of the first letter, it can be deduced that Neumann thought Frisch was the inventor of Prussian Blue and that he was not aware that Diesbach and Dippel were the two original inventors. In 1723 Dippel was still imprisoned on the Danish island of Bornholm (from 1719-1726). The existing information on Diesbach ends in 1716 with a letter from Frisch to Leibniz (5), and so it is not clear whether Diesbach was still working together with Frisch in 1723 on the Prussian Blue production in Berlin.

The Production of Prussian Blue According to Neumann

The preparation procedure for Prussian Blue which Neumann sent to Woodward (9) was the following (English translation after H. M. Powell (10):

Preparation of Prussian Blue sent from Germany to John Woodward, M.D. Prof. Med. Gresh., R.S.S.

Take 4 ounces of crude tartar (potassium hydrogen tartrate) and 4 ounces of dried crude nitre (potassium nitrate); powder them minutely and mix. Detonate them with charcoal, and you then have 4 ounces of extemporaneous alkali. While this salt is still hot it is finely powdered and 4 ounces of well dried and finely powdered ox blood is added.

These well-mixed components are placed in a crucible so that it is two-thirds filled. After it has been covered with a lid it is put on a fire and the crucible is piled round with coals so that it gradually begins to glow and the material takes fire and begins to burn without any violent outburst. The material is kept in this degree of fire until the flame and eruption slacken. The fire is then increased until the substance glows intensely and little further flame emanates from the crucible. Then remove the crucible from the fire and grind the material gently in a mortar; have ready 2 pints of boiling fresh water into which the material is thrown while still glowing and boil for the space of half an hour. The decoction is passed through a piece of linen and the remaining black material, on to which a further portion of water is poured, is once more placed on the fire, boiled, and filtered. This procedure should be continued until the saltiness and all bitterness have been washed out and the water remains insipid. Well press out all the liquors remaining in the linen and the material and when you have collected them all together, place again on the fire and evaporate down to 3 1/2 pints and keep for later use. (No. 1).

Then take 1 ounce of green vitriol, calcined gently to whiteness, and dissolve it in 6 ounces of fresh water; filter through paper and call this No. 2.

Then take 8 ounces of crude alum (KAl(SO_4), 12H₂O). Treat it with 2 pints of boiling water until complete dissolution of the alum and when this has been done, add it to the solution of vitriol No. 2 which is taken, boiling, from the fire, put into a pot of sufficient capacity and combined with the well boiling lixivium No. 1, previously set apart. There is a great effervescence of the contents and a green or greenish-blue colour appears. The liquid is poured alternately from one vessel to another during the effervescence, until it stops; then let it stand. It is then transferred to a piece of linen so that the liquors may flow through and the coloured substance remain on the linen. When no further water drips through it is removed from the linen with the aid of a wooden spatula into a fresh, smaller pot. Pour on to it 2 or 3 ounces of spirit of common salt and at once there appears a most beautiful blue colour. All is well stirred and allowed to settle overnight. Then a large quantity of fresh water is added and stirred with a spatula. After the material has settled the water is decanted and a fresh lot of water is poured over it, and this operation is repeated until all bitterness has been washed away and the water which flows out is insipid. When this has been completed, transfer the intensely blue precipitate to a taut piece of linen so that the water may gradually drain away. The pigment is dried in a gentle heat, and is then ready for use.

N.B. - In this procedure the calcination is of great importance because the sea-blue colour and the hidden sky-blue arise according as the calcination of the dried blood with the alkali is light, medium, or strong, and hence there is a diversity of colour.

The well-boiling lixivia are to be mixed one with the other in the most rapid manner.

According to his first letter to Woodward, Neumann discovered this procedure for the manufacture of Prussian Blue by his own experiments after he had acquired some knowledge about the principal reagents; and therefore, it is not necessarily the same method that Frisch and Diesbach used for their production in Berlin. An obvious difference from the procedure of the first Prussian Blue production by Diesbach and Dippel reported by Stahl (11) is that Neumann used a so-called extemporaneous alkali instead of potash for the calcination step with blood.

The Effect of Neumann's Letters

Woodward presented the contents of the second Neumann letter to the Royal Society on January 9, 1724. Obviously, the chemist John Brown (12), FRS initiated experiments to verify the production method for Prussian Blue and to perform some additional tests. He presented his results to the Royal Society on April 2 and April 16, 1724. Woodward published Neumann's Latin production method (9), without naming Neumann and without any further changes in the technique, in a paper in the *Transactions of the Royal Society* (7). Directly following this is a paper by John Brown, who describes his own experimental observations with this method and includes some new findings (13).

In 1725, one year after the publications by Woodward (7) and Brown (13), the French chemist Étienne-Francois Geoffroy reported that Prussian Blue was being produced in London in large amounts and that this Prussian Blue was of better quality than that which was



Figure 2. John Woodward, physician, geologist and naturalist in London, who in 1724 published the production method for Prussian Blue sent to him from Caspar Neumann (© The Royal Society).

produced by the Messrs of Berlin (14). He also published the details of Woodward's and Brown's publications in French, together with some of his own experimental results (14, 15).

Therefore, by the mid 1720s the knowledge of the manufacturing process for Prussian Blue was publicly available in Europe. A production monopoly was no longer in existence.

The Life of Caspar Neumann

Who was Caspar Neumann? Biographical information on Caspar Neumann can be found in several sources (e.g. Ref. 16), the most detailed and comprehensive in a German doctoral thesis from 1938 (17). A short summary of this information is given here, accompanied by some additional material from the archives of the Royal Society in London.

Caspar Neumann was born on July 11, 1683 in Züllichau (since 1945 the Polish Sulechov), a small town in the very eastern part of the German state Electorate of Brandenburg not far from the Polish border. The area on both sides of the boundary had a mixed German and Polish population. Therefore, Caspar Neumann was fluent in both German and Polish. His father was the merchant Georg Neuman (died 1695), his mother Rosina Neuman née Weichert (died 1693). After the early death of his parents, he was raised by his godfather Johannes Romke, the apothecary of Züllichau. He later became an apprentice of the apothecary profession under Romke. He finished his apprenticeship in May, 1701. During and after his apprenticeship he worked in and later also managed the apothecary shop of Romke in the small Polish town Kargowa (with the German name Unruhstadt) just across the border from Züllichau. Because of the Great Northern War (1700-1721), which in large part was fought in Poland, he left Kargowa in 1704 for Berlin, the capital of the Electorate of Brandenburg and, after 1701, also of the new Kingdom of Prussia.

In Berlin he began working for the apothecary Christoph Schmedicke (apothecary shop Black Eagle at the Kings Gate) in 1705. Soon afterwards he changed his employer and became a traveling apothecary of King Friedrich I (18) and served in this position until 1711. He was proposed for this post by the former traveling apothecary Conradi, who accepted a job directly in the Court Apothecary Shop. Neumann accompanied the king as an apothecary during his travels. During the time the king stayed in Berlin, Neumann worked in the Royal Court Apothecary Shop (19). Neumann was also an accomplished pianist and was required to give private concerts for the king. Through this endeavour, he became personally acquainted with the king. In 1711 Friedrich I sent him on an extended trip through Europe to improve his chemical and pharmaceutical education in several countries. After traveling through various parts of Germany, he moved to the Netherlands. There he visited Leyden, Utrecht, and Amsterdam. He stayed for an extended time with Boerhaave (20). In early 1713 he arrived in London. Shortly after his arrival he received a letter from Berlin informing him of the death of Friedrich I, whose successor, King Friedrich Wilhelm I (21), did not need his services anymore and would terminate any further payment.

He sought a new job in London and was fortunate to become employed by Abraham Cyprianus (22), a famous and wealthy surgeon and hobby-chemist with a private chemical laboratory. Caspar Neumann worked for the next three years, until 1716, in this laboratory. He also lived in the household of Cyprianus. In addition, he gave public lectures in chemistry. He became well acquainted with several English scientists, among them Newton (17) and Hans Sloane (23), as can be deduced from a later letter sent from Neumann in Berlin to Sloane in 1733. In this letter he wrote (24):

... I am sensible, Hon. Sir, how much I owe to you, for I gratefully remember that it was by your Recommendation not only that I was received into Your IIlustrous Society, but also, that during the 5 years which I lived at London in the House of Dr. Cyprianus, when I became acquainted with the family of Mr. Hadleys, I had leave to see your famous Collection of Natural Curiosities; for which favours bestowed upon me I find myself under eternal obligation.

Perhaps more importantly, during this time he also became acquainted with John Woodward, to whom he later sent the Prussian Blue letters. The content of this letter to Sloane, the help he received from several fellows of the Royal Society, and the fact that he was allowed to take part in meetings of this Society can explain Neumann's sense of being a debtor to the Royal Society, as he stated in his first Woodward letter in 1723.

Because he had a good and secure income now, Neumann decided to stay in England. To settle his affairs, he returned to Berlin in 1716 for a short time. Here he met the famous and influential Georg Ernst Stahl, physician and chemist, today best known for his contributions to the phlogiston theory. Stahl had been living in Berlin since 1715 and had been invited by King Friedrich Wilhelm I to serve as physician to the King. Stahl wanted to hire Neumann for the Court Apothecary Shop in Berlin. Therefore, he arranged with the king for Neumann to be offered a substantial position in the shop. First, however, Neumann would be allowed to finish his educational travels through Europe with his expenses again paid by the king. Caspar Neumann agreed. He then moved back to London, where he completed his studies. While still in London at the end of 1717, he received the news of the death of the second apothecary, Johann Caspar Conradi, of the Court Apothecary Shop. Half a year later, Memhard, the Royal Court Apothecary, also died. At this point, Neumann returned to Berlin by way of France and Italy, where he completed his educational travels at a rapid pace.

In early 1719 he arrived in Berlin and was immediately appointed as new Royal Court Apothecary, a post Neumann held until his death. At the beginning of his tenure in the Royal Court Apothecary Shop, located in a side wing of the Berlin palace, Neumann was responsible for delivering drugs and remedies to 8,000 persons at no cost or for a reduced fee. By 1732 this number had risen to about 20,000 (17). Caspar Neumann greatly improved the technical and organizational conditions of the Court Apothecary Shop.

Neumann became a member of the Royal Prussian Society of Sciences in 1721. In the same year he married Cornelia Maria, the widow of the former second apothecary Conradi. He had no children of his own but raised the two children of his wife and Conradi.

In 1723 the Collegium Medico-chirurgicum (25) was founded in Berlin. Neumann was appointed professor of pharmaceutical chemistry here in the same year. His lectures were delivered in German, not in Latin because he was (26):

being by a Royal Mandate are ordered to instruct the Youth here in what regards our institution in their mother-Tongue, which is the German: perhaps because the greatest part of the Students in Pharmacy and Surgery are unacquainted with the Latin.

Among his pupils at the Collegium Medico-chirurgicum was Andreas Sigismund Marggraf (27), who in 1751 first described a method of detection of iron in water by using the formation of Prussian Blue that occurred after the addition of hexacyanoferrate (so called blood lye) to water samples (28). In addition to instructing students, Neumann also gave public lectures in chemistry: "publick Lectures in Chymistry which I am oblig'd to make," as he wrote to Sloane (26). It was also in 1723 that Caspar Neumann wrote his letters on Prussian Blue to Woodward. In 1724 Neumann was appointed to the new higher Collegium Medici and was thereafter responsible for all apothecaries in the kingdom of Prussia. Proposed by Hans Sloane, he was elected to be a Fellow of the Royal Society in 1725. In 1728 he was elected to be the 400th member of the Leopoldina academy (29) with the cognomen Synesius. He was promoted in 1733 to the title Privy Councillor (Hofrat). In May, 1735 his wife died at the age of 48. About two years later, on October 20, 1737 he died at the age of 54. His stepson, Johann Caspar Conradi, was his successor as Court Apothecary.

Caspar Neumann was a typical apothecary-chemist of 18th century Germany (30). As a chemist, he concentrated on pharmaceutical and food chemistry. In his lifetime he wrote 24 publications, mostly in Latin but some also in German, in scientific journals or separately. He is not remembered as a discoverer of new elements or substances or as a very creative chemist. Rather, he was someone who collected the contemporary chemical knowledge and brought order to this collection.

For several decades after his death Neumann was still influential in the chemistry community, especially in Germany, because of his widely read books (31, 32). The content of these books, published posthumously, was an extensive summary of his lessons on chemistry. They were valuable because they contained the complete chemical knowledge of the time with a critical examination of many facts; and they were widely accessible because they were written in German instead of Latin. In England William Lewis (33) translated and rearranged these collected chemical works, which were subsequently published with additional material containing later discoveries and improvements in 1759 (34) (first edition). Dutch and French translations were also published.

Conclusions

The secret production process for Prussian Blue was revealed in two letters sent from Caspar Neumann in Germany to John Woodward in London. Extracts of these letters are preserved in the archives of the Royal Society. Soon after receiving the information from Neumann, Woodward published the description of the manufacturing process in the most prestigious scientific journal of the time. After Woodward's publication, Prussian Blue manufacture began in various European countries.

REFERENCES AND NOTES

- 1. Johann Jacob Diesbach was a Swiss pigment and dye producer living in Berlin at least between 1701 and 1716. Further information on him has yet to be discovered.
- 2. Johann Konrad Dippel (1673-1734) was a pietist theologian, physician, and alchemist. Between 1704 and 1707 he lived in Berlin and between 1707 and 1714 in Maarsen, Netherlands.
- 3. A. Kraft, "On the Discovery and History of Prussian Blue," *Bull. Hist. Chem.*, **2008**, *33*, 61-67.
- 4. Johann Leonhard Frisch (1666-1743) was a teacher at the Berlin gymnasium of the Grey Monastery from 1698, when he arrived in Berlin after several years of travel through Europe. Besides being a school teacher until his death, he was also very active in scientific studies. He joined the Berlin Society of Sciences in 1706. His scientific studies included works on mulberry trees and silk production, linguistic studies (e.g. German-Latin and German-French dictionaries), encyclopedic books on insects and birds, and, last but not least, for a certain time chemical studies including the improvement, manufacture, and sale of Prussian Blue.
- L. H. Fischer, Ed., Joh. Leonh. Frisch's Briefwechsel mit G. W. Leibniz, Georg Olms Verlag, Hildesheim, New York, 1976 (reprint of the book from 1896).
- John Woodward (1657-1728), a physician, naturalist, and geologist, was appointed professor of medicine in Gresham College in London and Fellow of the Royal Society from 1693.
- J. Woodward, "Praeparatio Caerulei Prussiaci ex Germania missa ad Johannem Woodward," *Philos. Trans. R. Soc.*, **1724**, *33*, 15-17.
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- H. M. Powell, "The Beginnings of Co-ordination Chemistry," *Proc. Chem. Soc.*, March, 1959, 73-75.
- 11. G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae*, Ambrosius Haude, Berlin, 1731, 280-283.
- 12. John Brown or Browne (?-1735) a chemist in London, Fellow of the Royal Society from 1721.
- 13 J. Brown, "Observations and Experiments upon the Foregoing Preparation," *Philos. Trans. R. Soc.*, **1724**, *33*, 17-24.
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- É.-F. Geoffroy, "Nouvelle Observations sur la Preparation de Bleu de Prusse," *Mém. Acad. R. Sci.*, 1725, 220–237.

- 16. "Kaspar Neumann," *Allgemeine Deutsche Biographie*, **1886**, *23*, 535.
- A. Exner, Der Hofapotheker Caspar Neumann (1683-1737); Ein Beitrag zur Geschichte des ersten pharmazeutischen Lehrers am Collegium medicochirurgicum in Berlin, D. Phil. thesis, Friedrich-Wilhelms-Universität, Berlin, Triltsch & Huther, Berlin, 1938.
- Friedrich von Hohenzollern (1657-1713) was the son of the Elector Friedrich Wilhelm (1620-1688) of Brandenburg (the Great Elector). In 1688 he succeeded his father to become Elector Friedrich III of Brandenburg. In 1701 he crowned himself in Königsberg (the modern Kaliningad in Russia) as the first King in Prussia (Friedrich I). He died on February 25, 1713 in Berlin.
- 19. The Court Apothecary Shop (Hofapotheke) in Berlin was founded in 1598 by Electress Katharina (1549-1602), the wife of the Elector Joachim Friedrich (1546-1608) of Brandenburg. It was responsible for delivering drugs and remedies gratis or for a reduced price to the elector (or later the King) and his family, to court employees, soldiers, all church and school employees, and to the poor, widows, orphans, prisoners etc. in Berlin.
- 20. Herman Boerhaave (1668-1738), a professor of medicine, botany, and chemistry at the university in Leyden. He was one of the most famous scientists of his time.
- Friedrich Wilhelm von Hohenzollern (1688-1740) was the son of the first King in Prussia, Friedrich I. In 1713, he became king himself (Friedrich Wilhelm I). Popularly known as the Soldier-King, he practiced rigid economy during his reign.
- 22. Abraham Cyprianus (~1656-1718), a Dutch surgeon and physician, living in London from 1696, a Fellow of the Royal Society from 1700, and Licentiate of the Royal College of Physicians.
- 23. Sir Hans Sloane (1660-1753), a physician, scientist, collector, Fellow of the Royal Society since 1685, and president of the Society from 1727 to 1741.
- 24. "Casper Neumann, dated at Berlin, to Hans Sloane," Berlin, April 16, 1733, Archive of the Royal Society, Early letters EL/N2/4.
- 25. The Collegium Medico-chirurgicum was an institution for the control and education of physicians and surgeons and for all other medical professions in Prussia. It was founded in 1723 in Berlin.
- "Concerning Ambergris by Caspar Neumann," Berlin, October 15, 1729, Archive of the Royal Society, Classified papers Cl.P/11ii/20.
- 27. Andreas Sigismund Marggraf (1709-1782) was an apothecary and chemist. From 1726 to 1731 he was apprentice at the Royal Court Apothecary Shop in Berlin. He also attended lectures on chemistry by Neumann in the Collegium Medico-chirurgicum. He is still well known for his discovery of sugar in beet roots in 1747.
- A. S. Marggraf, "Examen Chymique de l'Eau," Histoire de l'Académie Royale des Sciences et Belles-Lettres de Berlin, 1751, 131-157.

- 29. Founded in 1652 in Schweinfurt, Germany, the Leopoldina, located in Halle since 1878, is the oldest continuously existing scientific academy in the world. Since 2007 the Leopoldina has been known as the German Academy of Sciences.
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- 32. C. Neumann in C. H. Kessel, Ed., Chymica medica dogmatica-experimentalis: Das ist mit Experimenten erwiesene medicinische Chymie, Waisenhaus, Züllichau, 1749-1755.
- 33. William Lewis (1709-1781), physician and chemist, Fellow of the Royal Society, received the Copley Medal for his work on platinum in 1754.

34. W. Lewis, The Chemical Works of Caspar Neumann, M.D. Professor of Chemistry in Berlin, FRS etc., abridged and methodized: with large additions, containing the later discoveries and improvements made in chemistry and the arts depending thereon, Printed for W. Johnston, G. Keith, A. Linde, P. Davey and B. Law, T. Field, T. Caslon, and E. Dilly, London, 1759.

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