

# Rediscovery of the Elements

## Phosphorus



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Phosphorus historically represents a bridge between alchemy and modern chemistry. Phosphorus was discovered in 1669 by an alchemist searching for the philosopher's stone,<sup>1</sup> and a century later was used by Lavoisier to help usher in the era of modern chemistry.<sup>2c</sup>

**The Alchemists.** The person who discovered phosphorus was Hennig Brandt (ca. 1630–1710), a respected denizen of Michaelisplatz, an area in Hamburg, Germany (Figure 1). Trained in glass-making, Brandt married into wealth which supported his alchemical endeavors. In the vein of Aristotle's philosophy of qualities, Brandt's idea was that there must be a deep connection between yellow color of gold and of urine. In his private laboratory (Figure 2) he stumbled upon a procedure which produced small amounts of a white solid that gave off an eerie green color and spontaneously ignited, producing an acrid, garlic odor. The glow was even greater than that of *phosphoro di Bologna* (barium sulfate), gathered from the foothills of the Apennines a few years earlier by a cobbler named Vincenzo Casciarolo.<sup>2a</sup> The story of Brandt and the following history of phosphorus

has been recounted in a fascinating narrative by John Emsley<sup>3a</sup> (Figure 3).

The preparation of phosphorus by Brandt involved concentrating the urine to a thick paste, which was strongly heated to distill off the white material into water. The process worked because phosphates in the urine were chemically reduced by carbon produced by organic material in the urine decomposed by the heat. By collecting the distillate in water, the product would solidify and was prevented from reacting with the atmosphere.

Brandt worked secretly in his laboratory for several years in his vain attempts to transmute base metals into gold. However, the news of his discovery was soon circulating among citizens in Hamburg and other towns in Germany. Johann von Löwenstern-Kunckel (1630–1703), alchemist to Duke Franz Carl of Sachsen-Lauenburg, deduced the recipe, and actually claimed the discovery for himself. Kunckel would perhaps be known today as the discoverer of phosphorus, if it were not for Gottfried Wilhelm Leibniz (1646–1716, the co-inventor of the calculus), who was fascinated by public demonstrations of this strange *noctiluca* (night light). Learning of the true source of his phosphorus, Leibniz sought out Brandt, encouraged him in his work, and publicized his discovery.

The most popular "phosphorus shows" were presented by Johann Daniel Kraft (1624–1697), a silk and wool merchant from Dresden. Kraft purchased quantities of phosphorus from Brandt and traveled about Europe demonstrating the strange glowing substance to various audiences and royalty. The circuit tour of Kraft culminated in a visit in 1677 to Robert Boyle (1627–1691) in his London home; Boyle was fascinated and decided to study this new substance.

**The chemists.** Boyle, a Fellow of the Royal Society, is best known for his gas laws (1662) and for his definition of *element* in *The Sceptical Chymist* (1661). Although Boyle himself had searched for the philosopher's stone (as did other famous scientists, such as Isaac Newton), in contrast to the alchemists he undertook a scientific study of phosphorus. He took on a



Figure 1. The Michaelisplatz area is bounded by the two St. Michael churches. This is the main church, St. Michaelskirche (St. Michael's Church), Englische Planke 1, Hamburg, Germany (N53° 32.96 E09° 59.06). The original church was built 1648–1673, during Brandt's lifetime. To the east (300 meters) is Kleiner Michel (Little Michael's Church), built in 1606 (not shown; Michaelisstraße 5; N 53° 32.95 E09° 58.95). Both churches have experienced much damage and repair during their history.

young assistant from Saxony named Ambrose Godfrey-Hanckwitz (1660–1741), who extracted the vital piece of information from Brandt for making phosphorus: intense heat to effect the necessary reduction of phosphates. After Boyle lost interest in phosphorus, Godfrey developed a thriving commercial production of phosphorus, and soon was even transporting product to the European continent.

In 1734 Andreas Sigismund Marggraf (1709–1782)<sup>2c,f</sup> the famous Berlin scientist who preceded Martin Heinrich Klaproth<sup>2g</sup> (1743–1817, the discoverer of uranium) discov-

ered a more efficient method by heating concentrated urine with charcoal and red lead ( $\text{Pb}_3\text{O}_4$ ). However, production was still limited by the small amount of phosphorus in urine (1.4%) in urine.

A richer source of phosphorus was discovered in 1769 by the Swedish scientists Carl Wilhelm Scheele<sup>2d</sup> (1742–86, the codiscoverer of oxygen) and Johan Gottlieb Gahn<sup>2b</sup> (1745–1818, the discoverer of manganese). Scheele and Gahn independently discovered that bone could be reacted with acid to form phosphoric acid, which then could be reduced with charcoal. Since bone contains a large amount of phosphorus (dry bone is >50% calcium hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ), phosphorus could be produced in abundance.

The modern era of chemistry, marked by Antoine-Laurent de Lavoisier (1742–1794), included detailed combustion studies of phosphorus. These studies (along with those of sulfur and carbon) led to his understanding of the true nature of combustion—not a loss of hypothetical phlogiston, but instead a combination with “vital air,” or oxygen, from the atmosphere.<sup>2c</sup> Lavoisier included phosphorus in his list of 31 elements in his treatise.<sup>3</sup>

**Allotropes of phosphorus.** In 1841 Berzelius introduced a term “allotrope” to describe different modifications of the same formula, such as sulfur (rhombic and monoclinic) and carbon (diamond and graphite).<sup>4a</sup> Three years later he stated that there was a red modification (Figure 4) which formed slowly from white phosphorus at ambient conditions and did not reactive with the atmosphere.<sup>2f,4b</sup> However, it was not clear to others whether this red material was an allotrope or an oxide.<sup>5</sup> In 1848 it was shown<sup>6</sup> by Anton von Schrötter (1802–1875)<sup>7</sup> that red phosphorus and white phosphorus can be introconverted with no change in mass, and therefore red phosphorus was indeed an allotrope of white phosphorus. He prophetically suggested that red phosphorus might be utilized in the match industry; today it is used in safety matches. Schrötter, considered the discoverer of red phosphorus, performed his work at the Polytechnique Institute in Vienna, Austria, now the Technische Universität<sup>6</sup> (Figure 5).

Percy Williams Bridgman (1882–1961) of Harvard University, an expert in high pressure chemistry and a 1946 Nobel Physics Laureate, prepared a black allotrope<sup>8</sup> of phosphorus in 1914 (Figure 4). Other forms of phosphorus have also been prepared,<sup>1a,8</sup> but appear to be variations and/or intermediates of red and black phosphorus.

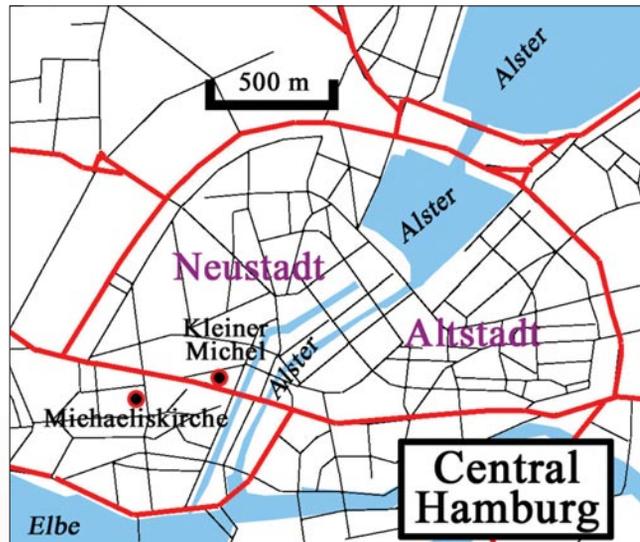
Molecular structures of these three main forms of phosphorus are shown in Figure 6. ○



Figure 2. TOP: Hamburg during the time of Brandt.

Hamburg was a primary member of the Hanseatic League; extensive trade was facilitated by the Elbe River (bottom), which flowed northwest to the North Sea 100 km away. The Michaelisplatz was in the Neustadt (new city), in western Hamburg.

BOTTOM: Central Hamburg today. The Medieval wall is now gone, but its former location can be traced by the expressway surrounding Central Hamburg. The Altstadt (old city) dates from 808 A.D. when its construction was ordered by Charlemagne, the Neustadt from the 1500s. The Alster River separates the Altstadt from the Neustadt.



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Figure 3. John Emsley (right), the raconteur of chemistry, shares his knowledge of chemical history with the authors. Emsley is well known for many books including *The Elements* and *The Shocking History of Phosphorus*, the primary source of material for this HEXAGON contribution.<sup>1a</sup>



Figure 5. Anton von Schrötter, discoverer of red phosphorus, performed his work at Technische Universität, Karlplatz, Vienna, Austria (then known as the Vienna Polytechnikum) (N48° 11.95 E16° 22.20). Insert: Bronze bust of Schrötter in the courtyard to the right. Another stone bust resides in the Schütte-Lihotzky Hörsaal (lecture hall).

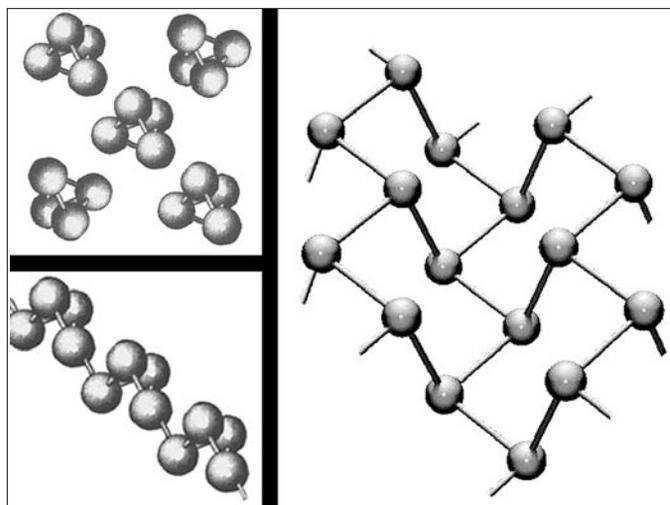


Figure 6. Upper left. White phosphorus, consisting of P<sub>4</sub> tetrahedral clusters, is soluble in carbon disulfide and was readily separated by Schrötter from insoluble red phosphorus. The most unstable allotrope, it ignites at 30-50°C. Lower left. Red phosphorus is a polymer generated from white phosphorus by the breaking of one P-P bond in each P<sub>4</sub> cluster. More stable than white phosphorus, it ignites 200° higher. Right. Black phosphorus is the most stable allotrope, but is less common.

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Figure 4. Three allotropes of phosphorus—(left to right) white, red, and black. From the authors elemental collection.

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