

Rediscovery of the Elements

Courtois and Iodine



James L. Marshall, *Beta Eta 1971*, and Virginia R. Marshall, *Beta Eta 2003*, Department of Chemistry, University of North Texas, Denton, TX 76203-5070, jimm@unt.edu

Bernard Courtois (1777–1838) serendipitously discovered iodine in Paris while reacting varec (ashes of seaweed) with sulfuric acid. He was using varec as a source of potash (potassium carbonate), necessary in the manufacture of saltpeter (potassium nitrate) used in gunpowder.

The history of saltpeter. The 7th century Taoist alchemists in western China stumbled onto a concoction of honey, sulfur, and saltpeter which caused smoke, fire, sparks, and thunder—called *huo yao*, or “fire drug”—thought to be the elixir of life.¹ We know the incendiary mixture today as gunpowder.²

By the mid-1200s, the Chinese discovery had spread to the Western world.¹ Roger Bacon (1214–1294) of Oxford recognized it as a mixture of “saltpeter, sulfur, and charcoal” (preferably of hazelwood), with the saltpeter in excess.² The Battle of Crécy in 1346, at the beginning of the Hundred Years War, may be marked as the formal introduction of gunpowder on the battlefield as “gonnes” were used beside the famous longbowmen.¹

In an attempt to understand the nature of gunpowder, Robert Boyle (1627–1691) studied gunpowder in a vacuum, generated by pumps

originally used in his gas law experiments. Boyle was puzzled by the behavior of gunpowder, which combusted in an evacuated jar just as it did in the open atmosphere, when heated by the sun’s rays concentrated by a magnifying glass.¹ Boyle did not understand that saltpeter (known today to be KNO_3) contained its own “air.” Carl Wilhelm Scheele (1742–1786) got his first hint of the nature of this supporter of combustion when he observed sparks as saltpeter was heated with oil, and he went on to discover oxygen.³ Today we understand the basic reaction of gunpowder to be $2 \text{KNO}_3 + 3 \text{C} + \text{S} \rightarrow \text{K}_2\text{S} + \text{N}_2 + 3 \text{CO}_2$. The evolved gases expand and serve as the propellant in rockets and guns.¹

Saltpeter (meaning “salt-rock”) is the most soluble of the nitrates and wicks up rapidly in soil; it was first observed in China where a climate of alternatively cold/hot wet/dry climates allowed it to form on soil surfaces.¹ In Medieval

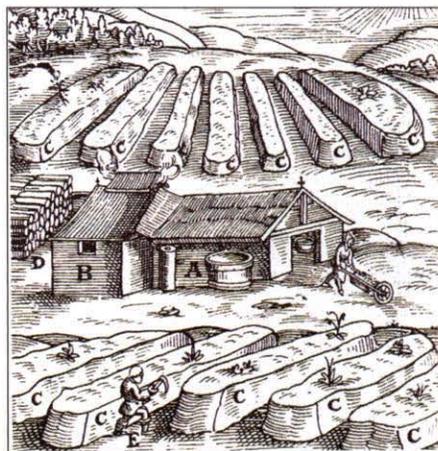


Figure 1. Saltpeter works as shown in a 1598 woodcut.¹¹ The rows of hills (C) were filled with manure, garbage, soil, blood, ash, and lime, and were periodically soaked with urine. The nitrogenous compounds released ammonia, which were oxidized to nitrates. After a year or so the “ripened” saltpeter beds were processed in the “refinery,” the work shed (B) (see Figure 2). The bucket (A) collected rainwater. A cord of wood (D) was used as fuel for the hearths in the shed. A saltpeter digger (E) would remove soil “ripe” for processing.

Europe, on stable and barn stone walls, saltpeter grew in the form of “blooms” resembling cotton tufts. Recent analyses show such growths of saltpeter are surprisingly pure, often greater than 95% KNO_3 .⁴ Saltpeter diggers—*Salpetergraber* in Germany or *Salpêtrier* in French⁵—soon learned to excavate soil about stables, pigeon cotes, manure piles, or barnyards to collect the saltpeter therein.

As the demand for saltpeter increased, the saltpeter plantation/refinery was born, called the *Nitrary* (*Nitrière* in French, *Nitriary* in German)⁵ (Figure 1). The manager of a nitrary would lay down a stratum of lime and cover with manure, garbage, corpses, and any other organic material, including a periodic dowsing with the urine of “drinkers of wine or strong beer.”¹ The major qualification of a nitrary manager was his ability to tolerate the incredible stench of his enterprise. After a few months the saltpeter diggers unearthed copious amounts of saltpeter-rich soil. An aqueous washing of the soil was reacted with ashes, filtered, concentrated by boiling, and cooled to produce white crystals of saltpeter. (Figure 2)

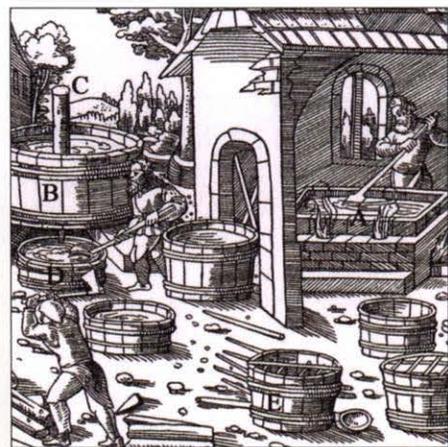


Figure 2. The refining of saltpeter in the shed (1556).¹² The “ripened” soil was leached in vat (B); the filtered solution was drained through plug (C) into collection vat (D). This filtrate was concentrated on hearth (A), then poured into crystallization buckets (E) with inserted copper sticks on which saltpeter crystallized as the solution cooled.



Figure 3. Southward view on Rue Monge in Dijon, France (N47° 19.12 E05° 02.02). The Académie de Dijon is to the left (51 Rue Monge); Courtois' home (where Bernard Courtois was born, 78 Rue Monge) is the gray building above the red automobile, just this side of the yellow half-timbered house. The Académie was founded in 1725 and moved to this Rue Monge location in 1772. (At this time, the street was called Rue Pontenart). Dijon is 250 km southeast of Paris.

Today we understand the chemistry of the process. Ammonia released from organic material is oxidized to nitrates. The lime (CaO) keeps the pH 7-8 required by the nitrifying bacteria. The product, calcium nitrate ("lime saltpeter"), is useless because it is hygroscopic and the resulting gunpowder would absorb moisture. Hence, the calcium nitrate is reacted with ashes (potash; potassium carbonate) to precipitate the calcium salts and leave a potassium nitrate solution: $\text{Ca}(\text{NO}_3)_2 (\text{aq}) + \text{K}_2\text{CO}_3 (\text{aq}) \rightarrow \text{CaCO}_3 (\text{s}) + 2 \text{KNO}_3 (\text{aq})$.^{4,5}

During the 1600s Great Britain found a cheap source of saltpeter—the East India Company could allow import of the commodity from India at one-quarter of the domestic cost.¹ (Note 1) France continued to produce its saltpeter from its home nitreries and itinerant saltpeter gatherers, but by necessity had to purchase some of its supply from Holland at an exorbitant price. Louis XVI (1752–1793) established the Gunpowder Administration in 1775, and as manager he appointed Antoin-Laurent Lavoisier (1743–1794), who promptly increased saltpeter production and improved the gunpowder manufacture process.^{3a} This self-sufficiency would be vital when Great Britain blockaded France during the French Revolutionary Wars (1792–1802) and the Napoleonic War (1803–1815).

Courtois in Dijon. Bernard Courtois was born in Dijon, France, the son of a wine merchant Jean-Baptiste Courtois (1748–1807?). The Courtois home was directly across the street from the Académie de Dijon (Figure 3), where the father won the position of chemistry demonstrator, hired by Louis-Bernard Guyton

de Morveau (1737–1816), a lawyer and chemist who founded the chemistry department at Dijon Academy.⁷ Guyton de Morveau is well known as one of the authors of the modern system of chemical nomenclature in 1787 (the others being Lavoisier,^{3a} Claude-Louis Berthollet (1748–1822),^{3c} and Antoine Fourcroy (1755–1809).⁶ In 1780 Jean-Baptiste was also assigned manager of the new Saint Médard Nitrary in Dijon (1.7 km east, on the outskirts of town) (Figure 4), one of the government-sponsored plantations created to cope with the saltpeter shortage.⁶ As a boy the precocious Bernard Courtois absorbed considerable chem-

ical knowledge and laboratory experience at the Académie laboratory and at the nitrary.

Courtois in Paris. In 1798, Bernard Courtois became a laboratory assistant at the École Polytechnique, arranged by Morveau who had moved to Paris in 1791 to become a member of the Legislative assembly and also a professor at l'École Polytechnique.⁶ At this time the École Polytechnique was located in the Palais Bourbon, directly across the Seine from the Place de la Révolution, today la Place de la Concorde, where Lavoisier was guillotined in 1794.^{3a}

At l'École Polytechnique Bernard Courtois worked with Fourcroy and Thénard (the discoverer of hydrogen peroxide, 1777–1857), then with Armand Séguin (1767–1835).⁷ Séguin is perhaps best known for serving as the human guinea-pig for Lavoisier's respiration studies; classic drawings by Mme. Lavoisier show him with the "gas-masks" in Lavoisier's laboratory at la Petit Arsenal.^{3a} In Séguin's laboratory Bernard worked with opium compounds, and apparently isolated morphine, although not formally acknowledged.⁶ Séguin delayed publication and was scooped in 1804 by Friedrich Wilhelm Adam Sertürner (1783–1841) of Paderborn, Germany, who gave the drug its modern name.⁶

In 1804, Bernard terminated his studies at l'École Polytechnique, which was becoming militarized upon Napoléon's edict and moved to its new site near the Panthéon.⁷ Bernard now assisted his father, who had moved to Paris in 1802 to set up a nitrary and had settled on Rue Saint Marguerite (today Rue Trousseau),⁶ about 1 km northeast of the Seine on the outskirts of town. Six years later, Bernard assumed ownership of his own nitrary another kilometer north



Figure 4. This is what remains of the largest and oldest (1582) plantation/refinery in Dijon—the Raffinerie des argentieres (N 47° 19.01 E 05° 03.25), formerly in the country, but now a residential neighborhood with no hint of the original nitrary. In the early 1800s there were always several nitreries in every city. Saint Médard (which Jean-Baptiste Courtois owned) was 600 meters north (N 47° 19.33 E 05° 03.36). Inset: Street sign expanded, "Street of the [saltpeter] refinery."

on Rue Rue Saint-Ambroise (Figure 5), where he remained 1810–1821.⁶ It was here that he discovered iodine.

The discovery of iodine. Potash was scarce because of the Napoleonic wars (1803–1815), and Bernard Courtois had resorted to varec imported from the Brittany and Normandy sea-coasts.⁶ One day in late 1811 while cleaning pots he accidentally discovered that concentrated sulfuric acid reacted with varec in an exothermic reaction to yield a violet cloud which condensed on a cold metallic or ceramic surface in the form of crystals with the color and luster of graphite.^{8a} Courtois performed some research on the crystals, and discovered a fulminating powder when he reacted the dark crystals with ammonia—he had produced nitrogen triiodide.^{6, 8a} Not being a regular member of the scientific establishment, he could not immediately publish his findings. In May 1812 he shared his experiences with his colleagues Nicolas Clément (1779–1842) and Charles Bernard Désormes (1771–1862), two scientists from Dijon who had studied at l'École Polytechnique when Bernard was there. Unfortunately, they were slow in their analysis of the new substance and did not report it to the Académie for 18 months.

Sir Humphry Davy (1778–1829) of London embarked on a two-year scientific tour of Europe in 1813, and because of his fame Napoléon granted him special permission to travel through France. While in Paris (October 15–December 23, 1813) Davy was given a sample of Courtois' "substance nouvelle" which he analyzed using the traveling laboratory chest he carried on all his journeys.⁷ Joseph Louis Gay-Lussac (1778–1850), a member of the elite Société d'Arcueil^{8b} who had formulated the law of combining volumes,^{8b} was motivated by this British intruder to initiate his own research. In a few weeks the two scientists had conducted detailed independent studies on this substance which had previously been shelved for 1½ years.

In December of 1813 there appeared⁸ in *Annales de Chimie* (the prestigious journal of the Académie des Sciences) several back-to-back papers on "une substance nouvelle dans le Varec" (a new substance from varec), which was called "l'iode" from the Greek word for "violet." These articles were authored by Courtois,^{8a} Gay-Lussac,^{8b} and Davy^{8c} (Courtois' paper was read by Clément, since Courtois was not a member of the Académie; he was identified only as a lowly "salpêtrier from Paris"^{8a}). Reflecting tensions between France and Great Britain, the (London) Royal Society delighted in noting (20 January 1814) that:^{9b}

"[Iodine] was discovered about two years ago; but such is the deplorable state of scientif-



Figure 5. This is the view northward on Rue Saint-Ambroise in northeast Paris (N 48° 51.76 E 02° 22.70). The home and Salpêtrière of Bernard Courtois where he discovered iodine, was on the left, present address is 31 Saint-Ambroise (old address 9), now the site of modern apartments. The plantation measured roughly 100 x 100 meters.

ic men in France, that no account of it was published till the arrival of our English philosopher there."⁶

One who reads these December papers of *Annales de Chimie*⁸ can begin to appreciate the fascination and confusion of the chemists as they tried to comprehend this "substance nouvelle"—this was half a century before the Periodic Table and the concept of chemical families. Iodine was difficult to categorize: It was very strange because it had the physical appearance and the heavy weight of a metal, but it dissolved in ether!^{8a} It behaved like oxygen or chlorine because it reacted with metals.^{8b, c} In fact, because of its odor,^{8a} iodine was originally thought to contain chlorine.^{8b} However, it was found to react with hydrogen gas to form not hydrochloric acid but a new acid (hydroiodic acid),^{8b, c} proven by its reaction with lead and silver nitrate to form unknown yellow salts (instead of white).^{8a} Ultimately, it was decided that it must be a "corp nouveau" (a "new body")^{8c} because it could not be broken

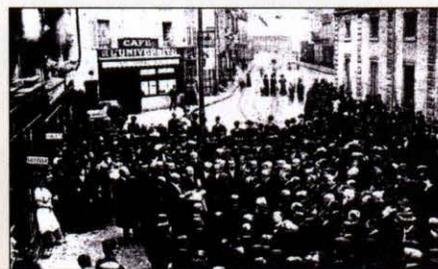


Figure 6. This photograph viewing northward on Rue Monge was taken on the 100th anniversary of the discovery of iodine (9 November 1911).⁶ The Academy is to the right; the crowd is facing left at the home of Courtois, where a plaque is being mounted.

down chemically, even in the presence of red-hot carbon.

In these December papers and others that followed,^{9b} vigorous competition between Gay-Lussac and Davy developed into bitter contention about who should be credited with what. Duplicate claims were published, even with regard to who named the new element. Gay-Lussac said he should be credited for naming it "l'iode." However, Davy maintained the correct name was iodine, in analogy to chlorine, which he had named in 1810 when he recognized its elemental nature.^{9a} (Previously, chlorine had been called "oxymuriatic acid," believed to be a compound of HCl and oxygen.^{9b}) Fortunately, in spite of heated arguments about proper recognitions, it was agreed that Courtois, who could have easily been lost in the shuffle, should be given credit for the initial discovery.^{8b, c}

In 1815 the Napoleonic Wars were over, and cheap Indian saltpeter became available.¹ Courtois turned his total attention to iodine, and with the help of Clément and Désormes developed methods for extracting iodine from seaweed in quantity.⁶ By 1820, the medicinal properties of iodine had become known and Courtois became a commercial manufacturer. In 1831, he was awarded the Montyon Prize by l'Académie for his contributions to medical science, but he never benefited financially from his discovery and he died penniless.⁶

On November 9, 1913, the scientific community commemorated in Dijon the 100th anniversary of the discovery of iodine by holding a banquet at the Dijon Académie and mounting a plaque on the old Rue Monge house (Figures 6 and 7).¹⁰ No bust or portrait was prepared for the celebration, because no likeness of Courtois was known,¹⁰ just as for Smithson Tennant (the discoverer of osmium and iridium)^{3d} (Note 2).

References.

1. J. Kelly, *Gunpowder*, 2004, Basic Books (Perseus Books Group), NY.
2. J. R. Partington, *A History of Greek Fire and Gunpowder*, 1999, Johns Hopkins University Press, Baltimore MD.
3. J. L. Marshall and V. R. Marshall, *The HEXAGON of Alpha Chi Sigma*, (a) 2005, 96(1), 8–13; (b) 2005, 96(1), 4–7; (c) 2006, 97(4), 50–55; (d) 2009, 100(1), 8–13.
4. U. Bretcher, "Ulrich Bretscher's Black Powder Page," <http://www.musketeer.ch/black-powder/salpeter.html>.
5. U. Bretcher, personal communication, Consulting Engineer, Kuster and Hager, Uznach, Switzerland.
6. L. G. Toraude, *Bernard Courtois et la Découverte de l'Iode*, 1921, Vigot Frères, Paris.



Figure 7. Plaque on the Courtois home.

Translation: "In this house was born on 8 February 1777 the pharmacist Bernard Courtois who discovered iodine in 1811."

7. P. A. Swain, *Bull. Hist. Chem.*, **2005**, 30(2), 103–111.
8. (a) B. Courtois, *Ann. Chim.*, **1813**, 88, 304–310; (b) J. L. Gay-Lussac, *op. cit.*, 311–318, 319–321; (c) H. Davy, *op. cit.*, 322–329.
9. J. R. Partington, *A History of Chemistry*, **1961**, Vol. IV, Macmillan, London (a) 51–57, (b) 85–90; (c) 636.
10. C. Guyotjeanin, *Revue d'Histoire de la Pharmacie*, **1995**, 42(2), 117–123. "Le Souvenir de Bernard Courtois," kindly furnished by Dr. Michel Pauty, Président de l'Académie des Sciences, Arts et Belles-Lettres de Dijon.
11. O. Guttman, *Monumenta Pulveris Pyrii*, **1966**, London.
12. H. L. and L. H. Hoover, English translation of G. Agricola, *De Re Metallica*, 1912, London; 1950 edition., Dover, New York.

Notes.

Note 1. Later, when Indian saltpeter became excessively expensive, Chilean saltpeter could be exploited. However, this South American commodity is mainly sodium nitrate, which is inferior because it is hygroscopic.¹ Bird and bat guano have also been rich sources of ammonia. With the development of the Haber process (the combination of nitrogen and hydrogen gas to form ammonia by Fritz Haber 1868–1934) in 1913,² there was no further need for organic sources of ammonia for the munitions industry.

Note 2. Careful research by French historians, including detailed interviews with descendants, has verified that no drawing, painting, or other likeness has survived of Bernard Courtois.¹⁰ However, recently a photograph(!) of Bernard Courtois has been posted on Wikipedia which is nonsense for such an early date. The authors are working to correct this error which has been repeated on several websites. This cautions one to be very wary of information on websites, even the usually reliable Wikipedia, which contain much unverified and redacted material.