

Bernard Courtois

The discoverer of iodine

Jaime Wisniak

Abstract

To Bernard Courtois (1777-1838) we owe the discovery of iodine and perhaps also of morphine. He lacked formal studies in chemistry and other sciences but received practical training in these areas from his father. A brilliant observant spirit led him to iodine, and as a consequence, providing Humanity with powerful therapeutic tool. He never patented his discovery and died in complete poverty.

Resumen

A Bernard Courtois (1777-1838) le debemos el descubrimiento del yodo y tal vez de la morfina. No recibió educación formal en química ni en ciencias, pero su padre le proporcionó entrenamiento práctico en estas áreas. Un espíritu brillante e intuitivo lo guió hacia el yodo y, como resultado, a proveer a la humanidad con una potente herramienta terapéutica. A consecuencia de no haber patentado su descubrimiento, murió en total pobreza.

Life and career (Cap, 1851; Richter, 1907; Toraude, 1921)

Bernard Courtois was born in Dijon on February 7, 1777, the son of Jean-Baptiste Courtois and Marie Bled. He was the fourth of seven children. At the time of Bernard's birth his father worked as a *préparateur* (responsible for the practical work with students) for the Chemistry course that Louis-Bernard Guyton de Morveau (1737-1816) gave at the *Académie de Dijons*.

The *Académie de Dijons*, founded in 1736, was initially installed in a hotel, where Jean-Baptiste worked as a valet. After the sale of the hotel and installation of the Academy, Jean-Baptiste requested a job from Guyton de Morveau and was employed as his laboratory helper. He was very diligent and promptly was employed as *préparateur*. He soon began preparing table vinegar that became popular because of its purity; Jean-Baptiste distilled it on glass and clay vessels instead of copper ones, as done by others. Production of vinegar was an important ac-

tivity in Dijon, as part of the manufacture of the famous Dijon mustard. Jean-Baptiste was a smart merchant; besides vinegar he also manufactured carbonated water, inks, different chemicals, sticking plaster, and white paint. He came into the idea of replacing the lead carbonate used in cellar paints, by zinc oxide, which was not blackened by sulfides and remained white.

In 1777 Guyton de Morveau and Champy, the commissar for gunpowder and saltpetre of Bourgogne, established a society to build a *nitrière artificielle* for manufacturing potassium nitrate. The facilities opened on 1780 under the supervision of Jean-Baptiste Courtois. Eventually, Jean-Baptiste bought the *nitrière* and abandoned his job at the Académie. He made the *nitrière* successful and became rich.

We can already see that Bernard spent his youth in an environment of chemical activities. His father put Bernard as an apprentice under Frémy, a pharmacist at Auxerre, where he stayed for three years. After this apprenticeship, Bernard Maret, his godfather, brought him to Paris, where Guyton de Morveau was the Director of the *École Polytechnique*, and at the pinnacle of his scientific career, Guyton de Morveau placed Bernard Courtois to work in the laboratory of Antoine-Francois Fourcroy (1750-1809).

In 1799 Bernard was called to serve as a pharmacist in Army hospitals, where he fulfilled several tasks although he did not have the pertinent pharmacist diploma (as Toraude explains, the Health Schools, constituted in 1794, were in charge of preparing the personnel appropriate for the Army needs and started issuing certificates of capacity only after 1798). There he served for one year and afterwards he entered the laboratory of Louis-Jacques Thénard (1777-1857).

Around 1802 he joined the laboratory of Armand Séguin (1767-1835) as part of the group investigating opium. While performing this task, Courtois isolated a crystalline material having alkaline reactions and capable of combining with bases. This substance, the first alkaloid to be known, was *morphine*. Courtois discovered that morphine had alkaline properties but was not able to go further and decide if these were due to the reagent used for its preparation (ammonia) or proper of the compound.

*Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.

Correo electrónico: wisniak@bgumail.bgu.ac.il

On December 24, 1804, Séguin communicated to the Institute the memoir of his collaborator, which was incorporated into the Annals of the Institute only ten years later (Séguin, 1814). The opium alkaloid was so clearly indicated that when in 1816 Friedrich Wilhelm Sertürner (1783-1841) published his research results about opium Louis-Nicolas Vauquelin (1763-1829) did not hesitate to claim in Séguin's favor the priority of the discovery. But Séguin's work was really the fruit of the clever research efforts of Courtois.

Sertürner named *vegetable alkali* the crystalline substance discovered by Courtois, which was not other than *morphine*. With his work Courtois had revealed the existence of a new series of substances that today we call alkaloids.

Toraude (Toraude, 1921) asks the question: How come that Courtois did not become a well-known scientist in spite of his ample knowledge of Chemistry? Toraude believes that it was because of the lack of self-confidence exhibited by Courtois; it seems that he was lacking formal studies, including the secondary level. He thus committed with morphine the same error he would commit later with iodine: he did not pursue his findings to the end and did not assert his claims to the discovery.

Ultimately, the ways of Séguin and Courtois ways separated. After the Revolution Séguin became very rich by becoming the official provider of hide and leather for all the Revolutionary Armies. Eventually Napoleon forced him to return part of his fortune and, towards the fall of the Empire he was thrown into jail. Courtois, on the other hand, involved himself in the production of saltpetre in his father's business that had meanwhile moved to Paris.

In 1808 Courtois married Madeleine-Eulalie Morand; their only son, Louis, was born in 1816 and passed away, a bachelor, in 1866.

In 1804 Bernard left Séguin's laboratory to establish a *nitrière artificielle*, based on production methods that he had developed and to which he continued to introduce significant improvements. Here he prepared sodium nitrate in large scale, by decomposing calcium nitrate with the soda obtained from varech (varech soda).

The name *varech* is generally given to all the plants left by the tide that live in the sea at a low depth. The word has many explanations, for example, it is said to be derived from an old Norman word that originated from the English *wrack* or *wreck* (sea wreck). For others, it originates from a Scandinavian expression meaning literally *thrown by the sea*. The

difference between both explanations is marked, but the sense remains the same. The orthography of the word has changed. At Courtois's time it was written either vareck or varec. The term varec was also used to design the soda that was prepared from it. Today, the word is used to describe certain phanerogams, among them *Zostera marina* L., used for the manufacture of vegetable fibers for packaging and upholstery.

The plants used by Courtois were brown algae, particularly fucus that the low tide would deposit on the shore; the *goémons* (seaweed) included various species of Fucus and Laminaria, depending on the sea depth from which they were collected. During Courtois's time the processors of soda gathered particularly the black goémon formed by the Fucus and the Ascophyllum (*Fucus nodosus*) varieties. All the algae species contained, after calcination and treatment, the carbonates, chlorides, sulfates, bromides and iodides of sodium, potassium, magnesium, and calcium.

Collection of the various goémons was subject to very severe administrative regulations because of accusations that it affected the income of fishermen as well as created serious pollution problems.

The production procedure was very simple. The algae were first incinerated at the collection place and the ashes sent to the factory to be lixiviated. The incineration was done in a longitudinal pit excavated on the ground of the shore; the bottom of the pit was covered with flat stones, and to this were added the algae that had been dried before. Fire was started with furze, little by little, to assure the combustion of the whole batch. The ashes thus formed constituted, after the hot fusing and kneading, the saline of varech, rich in potassium and sodium salts and containing a certain quantity of iodides and bromides. Sodas of good quality contained about 0.8 to 1.0 percent of iodine.

Lixiviation was done at the production site. The blocks of ashes were subjected to the action of water that dissolved the soluble components. The lixiviates were concentrated and evaporated; sodium chloride precipitated first, followed by potassium chloride and sulfate. At this point the mother liquor had a density of about 55°Bé and contained the iodides of sodium and potassium, the sodium chloride that had not crystallized, sodium sulfate and carbonate, cyanides, polysulfides, as well as the sulfites and hyposulfites that originated during the increased reduction of the sulfates during the calcination process.

The reader interested in a detailed description of the varech industry is directed to the works of

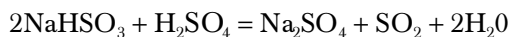
Clow (Clow, 1992) and Clow and Clow (Clow and Clow, 1947).

Courtois, like all later manufacturers, used sulfuric acid to destroy the sulfur derivatives. Towards the end of 1811 he observed that after treatment with sulfuric acid, the mother liquors of saltpetre led to the formation of a crystalline residue that had the remarkable characteristics of generating a violet vapor under the action of heat and having a metallic appearance at room temperature. In addition to the violet vapors, he noticed that the heated copper vessels used in the production process would become promptly perforated. These two observations took place in 1812.

Courtois's curiosity was piqued by this discovery and did some preliminary tests on the new substance. He found that it melted at about 70°C generating violet vapors and was unaffected by high temperature, carbon, and oxygen. On the other hand, it reacted with hydrogen forming something like an acid; phosphorus yielded the same result. He tried its action on several metals and found that it attacked them without effervescence. It also combined with oxides yielding products that were soluble in water.

Today we understand that the combined action of heat and sulfuric acid led to the transformation of hydroiodic acid to iodine and that the violet color of the vapor revealed the presence of iodine (by then unknown) to the observant eye of the manufacturer. Gay-Lussac wrote later, about this observation: "Dans les soudes de vareck, où il y a beaucoup des sulfites sulfurés, l'iode est à l'état de acide; il ne se manifeste dans les eaux-mères de ces soudes que lorsque les sulfites sulfurés sont détruits (in vareck soda, that contains large amounts of sulfates and sulfites, iodine is in an acid form and manifests itself only after the polysulfides have been destroyed) (Gay-Lussac, 1813a)."

Today we know that the reactions are



Courtois wanted to continue his research but he had only limited facilities at his service. In addition, he was not so confident on himself and his industrial activities did not leave him much free time. Thus towards 1813 he requested from two of his Dijon compatriots, Charles-Bernard Desormes (1777-1862), a chemical manufacturer and politician, and Nicolas Clément-Desormes (1779-1842), a physician, che-

mist, and professor at the *Conservatoire des Arts et Métiers*, to continue his research.

On November 29, 1813, Clément presented to the Institute, in Courtois's name, the discovery of the new element (Clément, 1813) and in two sessions held on December 6 and December 20 of the same year, Gay-Lussac established in two brilliant works the relation of the new body with the other elements and named the new substance *iode*, from the Greek $\iota\omicron\epsilon\iota\delta\eta\zeta$, violet, because of the color of its vapors. When Clément communicated his results to the Institute, Gay-Lussac had already initiated his research on iodine. Clément announced that Gay-Lussac had demonstrated that the acid (HI) was the result of the direct combination of iodine and hydrogen, and that further experiences by Gay-Lussac had shown that iodine was a simple substance, similar to chlorine and like it, it gave origin to particular acids when it combined with hydrogen, phosphorus, sulfur, etc.

Gay-Lussac's results are contained in three works (Gay-Lussac, 1813a; 1813b, 1814); the first is entitled *Sur un Nouvel Acide Formé avec la Substance Découverte par M. Courtois* (About a new acid formed with the substance discovered by Courtois) (Gay-Lussac, 1813a) read at the Institute on Monday, December 6, 1813; the second was *Note sur la Combinaison de l'Iode Avec l'Oxygène* (A note about the combination of iodine with oxygen) (Gay-Lussac, 1813b) read at the Institute on the following December 20, and particularly the third, *Mémoire sur l'Iode* (Memory about iodine) (Gay-Lussac, 1814), read by the author to the Institute on August 1, 1814. This last memoir is a considered a master piece, it contained 155 pages and in the late 19th century Wilhelm Ostwald (1853-1932) selected it as a prime example of a classic in science; he said that it was "one of the first and one of the best monographs of all time on a single element and its most important compounds, and as such it has served as a model for many later pieces of research."

At this stage an unfortunate incident took place. Courtois was a very good and honest man and without reservations distributed samples generously among his friends. Clément thought it appropriate to show his sample to Humphry Davy (1778-1819), who was then visiting France. Impressed by the especial properties of the new material, Davy made a rapid study of it and sent a letter entitled *Sur la Nouvelle Substance Découverte par M. Courtois dans le Sel de Vareck* (About the new substance discovered by Courtois in the salt of vareck) (Gay-Lussac, 1813a) to

Georges Cuvier (1769-1832), the permanent secretary of the *Académie*.

In this letter, read at the Institute on December 13, 1813, five days after the reading of Gay-Lussac's first note, Davy reported his experimental results on the combination of the new material with sodium, potassium, metals, and certain gases (Gay-Lussac, 1813a), and confirming some of the results that Gay-Lussac. Davy stated that after eight days of hard experimental work he had come to the conclusion that iodine was a simple body and that the acid obtained by the action of phosphorus on it was a hydrogenated compound.

In another letter, this time to his brother John (March 18, 1814), Davy wrote: "Iodine was for two years in an embryonic state. I went to Paris, Clément requested from me to examine it, he believed that it was a compounded body, produced from muriatic acid. I have worked with it for some time and determined that it is a new compound that produces a particular acid when it combines with hydrogen. I approached Gay-Lussac, Ampère, and other chemists. The first immediately took the word of the Lord out the mouth of his servant', and treated the subject as he had treated potassium and boron. The *Mémoire sur l'iode* that I have sent to the Royal Society has been written with the approval of M. Clément and a note published in the *Journal de Physique* establishes my priority rights (published on December 12, 1813)."

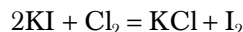
Davy realized immediately that he had in his hands a new element and his conclusion was reported in a derogatory manner in the British journal directed by William Nicholson (1753-1815) and Alexander Tilloch (1759-1825): "It appears that his gas (iode) was discovered about two years ago, but such is the deplorable state of scientific men in France, that no account of it was published until the arrival of our English philosopher there (Anonymous, 1814).

The haste that Davy had shown to publish his first results, after the first communications at the Institute, and the insinuation of British journals that tended to give to Davy the priority of the discovery, irritated Gay-Lussac who saw it proper to reestablish the facts in his extensive memoir about iodine, published in August of the following year.

On December 27 of 1813, Jean-Jacques Colin (1784-1865), a *répétiteur* at the École Polytechnique, read also a note related to certain new combinations of iodine, a work done under the guidance of Gay-Lussac (Colin, 1814).

Activity was intense not only on the chemistry of iodine but also on the search of the best raw material for its production. Henri-François Gaultier de Claubry (1792-1878), a contemporary of Courtois, investigated in 1814 the content in iodine of the different algae and arranged them in the order *Laminaria saccharina*, *Laminaria digitata*, *Fucus serrata*, *Fucus vesiculosus*, *Holidrys siliquosa*, and *Chorda filum*. *Laminaria digitata* was the richest and *Chorda filum* the poorest (Gaultier de Claubry, 1814). Gaultier de Claubry recommended extracting iodine directly from *Laminaria saccharina*, by drying, grinding, and treatment with sulfuric acid. He indicated that this procedure would avoid the long procedure of treating the mother liquor of vareck. He also mentioned that the sugar of fucus was completely different from that obtained from cane but seemed to be similar to the one obtained from *Allium cepa*. Today we know that large brown algae contain mannose and not glucose. Gaultier de Claubry is also remembered because together with Séguin they discovered the blue coloration of starch with iodine. They claimed that iodine was present in algae in the form of potassium iodide.

After the discovery of iodine, Courtois, with the help of Charles-Bernard Desormes (1777-1862) and Nicolas Clément-Desormes (1779-1842), looked for a practical way to extract iodine in large quantities. For this purpose he considered using chlorine to decompose the mother liquor of calcinated brown algae, previously purified with sulfuric acid, by the reaction



The procedure took place in clay vessels, having a capacity of 100 to 250 L, provided with three tubes, one for feeding chlorine, the other for discharging it, and the third for mixing. The iodine thus produced, somewhat wet, was crude iodine. It was sublimated and then transformed into iodides.

While Courtois' discovery was developing in a brilliant way, not so were the fortunes of the discoverer. In 1815 French ports were opened to the import of many products, among them, saltpetre from India, a fact that meant the ruin of the French *nitrières artificielles*. Courtois, who had invested all his fortune in this industry, was completely ruined. He tried to improve his lot by manufacturing iodine, but the market was far from enough to offer the appropriate benefit. Courtois was able to manufacture iodine only in small amounts, selling it for 600

francs per kilogram. The growing interest on iodine as a therapeutic agent led many to think about constructing an industry for large-scale production. Thus, in 1824, the baron d'Aigremont, under the advise of Clément-Desormes, established the first factory, and put Tissier, his future son-in-law, to manage it. Within a few months Tissier had produced 120 kg of iodine prized at 200 francs per kilogram. Shortly afterwards, Tissier became associated with Couturier, a manufacturer of refined soda in Cherbourg, and started manufacturing potassium chloride and sulfate, and other salts contained in the varech ashes. In this new facility they were able to produce 400 kg iodine per year, at a price of 100 francs per kilo. By 1830 the industry was also producing potassium iodide. These low prices meant the ruin of Courtois, who in 1835 was forced to sell his premises to Couturier.

According to Matignon (Matignon, 1914) by 1873 there were nine installations in France, treating 20,000 tons/year of varec and producing 50,000 kg of iodine.

Courtois was left in a very precarious economic situation, in which he remained until his death. After selling his industry he survived by occupying himself as a broker. Courtois fought with resignation against the attacks of age, illnesses and sorrow. In June 23, 1831, through the generous initiative of Thénard, the *Académie des Sciences*, awarded Courtois 6,000 francs from the Montyon prize. This prize was established to honor those who had perfected the art of curing. Prizes of 4,000 and 6,000 francs were also awarded to Coindet for applying iodine for the treatment of goiter, and to Lujol for having specified the precise medical procedure (Matignon, 1914). In the same year (1831) Daguerre brought into attention the action of light of silver plates that had been previously exposed to the action of iodine vapors; a discovery that would lead to the development of photography.

Towards the end of his life, Courtois dedicated himself again to chemical research. Opium, which was frequently used for the treatment of maladies, was again a subject of his work. It is very probable that he foresaw *codeine*, because he announced with confidence that morphine was not the only alkaloid contained in opium.

Courtois died on September 27, 1838, at the age of 62, without honors and leaving his fifty-nine year old widow with no more than a famous name. Of the 6,000 franc of the prize awarded to him in 1831, nothing was left at the time of his death. As

written in a short obituary published in the *Journal de Chimie Médicale, de Pharmacie, de Toxicologie*, 596 (1838), "had Courtois taken a patent for his discovery he would have probably died very rich." The economic situation was so bad that his widow was unable to buy him a permanent tomb in the *Cimetière du Nord*. He was buried there, on September 29, 1838, in a temporary grave, for the period of five years.

Courtois's widow went on to earn her living as a lace woman. She passed away on January 11, 1859, at the age of seventy.

On November 9, 1913, on the centenary of the discovery of iodine, the city of Dijon put a commemorative plaque on Courtois's house, and a year later a street was named after him.

First works on the properties and chemistry of iodine

As mentioned before, the discovery of iodine led to a flurry of papers, the most important of them being the four that were published in 1813, one after the other, in the journal *Annales du Chimie*, and involving the principal players, Courtois, Clément, Davy, and Gay-Lussac. Here we will give a short description of their contents to show the excitement of the discovery and the vast amount of information collected in a short period. The actual result of the chemical reactions studied is written in parenthesis.

The first publication was that of Clément, announcing Courtois's discovery of a new substance (Clément, 1813).

According to Clément, the mother liquor of the lyes of vareck contained a large amount of a singular and curious substance that could be easily separated by adding sulfuric acid and heating. The substance precipitated as a bright black powder and generated a violet vapor, which condensed in the form of crystalline laminar sheets, very brilliant, and having a brightness equal to that of crystallized lead sulfide. The substance looked like a metal, had an specific weight about four times that of water, a smell similar to that of *oxymuriatic acid* (chlorine), and it stained paper and the hands red-brown. It was neither acid or alkaline and volatilized at about 75°C. It sublimated easily, producing very bright laminar sheets that were a little soluble in water, much more in alcohol, and very much in ether. Heated alone, or in the presence of air or carbon did not affect it, but hydrogen gave place to a substantial change. When a mixture of iodine vapors (wet or dry) and hydrogen flowed through a tube heated red, the violet color

disappeared almost completely and a colorless gas was recovered, part of which dissolved in water. The water solution obtained was acid and had a dark red color.

Clément considered that the reaction of hydrogen with iodine was probably the most remarkable of the observed properties and would probably shed light over its nature. He indicated that Gay-Lussac considered that the acid was the result of the direct combination of hydrogen and iodine (HI).

The action of phosphorus on iodine was very violent, it took place instantly at room temperature, was very exothermic and generated a large quantity of gas, which proved to be very acid and very flammable (HI). If the iodine was wet, the reaction of phosphorus and iodine produced a red substance (PI₃). A similar behavior, although less energetic, was observed with sulfur.

The new substance was strongly active with metals (mercury, iron zinc, tin, and antimony); it combined with them and their oxides at room temperature and the product of the reaction was soluble in water. Gold and platinum were the only metals that do not combine with it.

Iodine combined very easily with sodium and potassium hydroxide. The action of ammonia gave place to an explosive powder (NI₃) that yielded the violet color at the time of the explosion.

Clément finished his remarks reporting that Gay-Lussac believed that iodine was a simple substance analog to chlorine, and like the latter, it gave place to particular acids when combined with hydrogen, sulfur, and phosphorus.

The following paper was Gay-Lussac's first note (Gay-Lussac, 1813a) where he repeated some of the previous observations and added some new details. It pointed out that the new substance, which could be named iodine, had the electrical properties of oxygen and *acide muriatique oxygéné* (chlorine). Heating of the wet product of reaction between iodine and phosphorus (phosphorus iodide, PI₃) it generated a large amount of acid fumes and phosphorous acid (H₃PO₃).

The new acid (HI) was colorless in the gaseous state with a slight odor like HCl, it fumed in the presence of air, was easily absorbable in water, and with chlorine yielded a purple vapor (I₂). Under the action of a battery, a water solution produced iodine at the positive pole. Hydrogen sulfide discolored iodine promptly and transformed it to the acid state with the simultaneous precipitation of sulfur (H₂S + I = 2HI + S).

Sulfurous acid (SO₂) converted iodine into an acid (HI) and became sulfuric acid. Phosphorus acid and the *sulfites sulfurés* (hyposulfites) were also capable of generating the new acid. From these results it could be concluded that vareck sodas contained *sulfites sulfurés*, that the new substance was in the acid state, and that it manifested itself only after the *sulfites sulfurés* had been destroyed.

From the above description a comparison with chlorine and hydrogen chloride was unavoidable and it seemed that iodine played in nature for some substances the same role as oxygen for others. All the phenomena could then be explained by assuming that *iodine was an element* and that it formed an acid when combining with hydrogen. A convenient name for the new acid was *acide hydriodique* (hydroiodic acid).

The following text was the first note by Gay-Lussac (Gay-Lussac, 1813b) where he reported that he had prepared the new acid formed by hydrogen and iodine, as Davy had done, as well as an explosive salt (potassium iodate, KIO₃) by reacting iodine with potassium hydroxide. This new salt was a white powder, soluble in water; when mixed with sulfur and carbon it exploded mildly, yielding a large amount of oxygen gas, a reaction similar to that of potassium chlorate. Gay-Lussac tried to decompose the explosive salt using acids; with HCl, it formed *l'acide oxymuriatique oxygéné* (HCl) and a combination of iodine and chlorine (iodine chloride). Treatment with hot sulfuric acid generated a gas containing oxygen and iodine. The explosive salt of baryte (barium iodate) was prepared in a similar manner; treatment of the salt with sulfuric acid yielded a new combination of iodine with oxygen (iodic acid, HIO₃). Addition of sulfurous acid (SO₂) caused iodine to precipitate and formation of sulfuric acid (2HIO₃ + 5SO₂ + 4H₂O = I₂ + 5H₂SO₄).

According to Gay-Lussac, iodine was capable of forming two remarkable acids, one where it was combined with hydrogen and the other where it was combined with oxygen. The new acid, which he proposed calling iodic acid, seemed to have very strong affinity because with baryte it formed a slightly soluble salt that was hardly decomposed by sulfuric acid.

In the following note, Davy (Davy, 1813) stated in belief that the substance found by Courtois was a new body (element) and that it reacted with wet phosphorus to form a new compound with hydrogen (HI). Treatment of the new acid with potassium yielded the same product as the direct treatment of

Courtois' substance with potassium. In addition, one volume of hydrogen was produced for two parts of the acid gas employed ($2\text{HI} + 2\text{K} = 2\text{KI} + \text{H}_2$).

The new acid reacted with metals, including mercury, yielding a compound of the metal and the substance and releasing hydrogen. The acid gas combined with an equal volume of ammonia gas and showed a strong attraction for water. The metallic combinations (iodides) or phosphoric combinations (phosphor iodides) reacted rapidly with pure ammonia. Heating of the resulting product did not generate oxides or oxidized bodies.

Davy indicated that he was unable to find chlorine, hydrogen chloride, or oxygen in the new acid. The new acid combined rapidly with chlorine or HCl forming a crystalline yellow solid (iodine trichloride, ICl_3 , that crystallizes in yellow needles). This solid was very volatile and very soluble in water. Its aqueous solution reddened immediately the vegetable blues and destroyed them immediately. This action was similar to that of chlorine and *acide muriatique suroxigéné* (HClO_3). The new substance resembled oxygen by the nature of the compounds it formed with metals and because chlorine displaced it from its combinations.

Another interesting reaction was with alkalis because it formed simultaneously binary and triple combinations (simultaneous formation of iodide and iodate, $6\text{KOH} + 3\text{I}_2 = 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$). The oxygen of the alkali combined totally with a portion of the substance to yield a ternary compound (iodate) that was little soluble and precipitated in crystalline form. The binary compound formed with the metal of the alkali (iodide) remained in solution. Heating the ternary compounds resulted in the release of large amounts of oxygen ($2\text{MIO}_3 = 3\text{O}_2 + 2\text{MI}$) leaving a residue (iodide) composed of the new substance and the metal. All the ternary salts detonated with carbon and other combustible substances although they do not abandon their oxygen as fast as the *sur-oxymuriates* (chlorates) and could probably be used as nitre.

Desormes and Clément had described the explosive powder that the new substance produced with ammonia; Davy believed the explosive product was formed by the new substance and nitrogen (nitrogen iodide, NI_3). Treating the explosive with ammonia yielded a salt (ammonium iodide, NH_4I) containing ammonia, and the new acid (hydrogen combined with the new substance). The explosive compound was strongly similar to the one

produced by the combination of ammonia and chlorine.

Davy tried to estimate the atomic weight of the new substance by determining the proportion in which it combined with sodium and potassium. His results indicated that the proportion was more than double that with chlorine. Considering oxygen as 15 and chlorine 67, it was between 160 and 170. This proportion and its solid state explained why its reactions yielded little heat and rarely light.

Based on its color, brightness, and weight, the new substance could be considered a metal, but its chemical energy classified it together with oxygen, chlorine, and fluorine. The substance did conduct electricity and its energy was negative respect to metals but positive in relation to chlorine. Electrifying (electrolyzing) an aqueous solution of the acid composed of chlorine and this substance (ICI), it moved to the negative pole, while in its alkaline combinations I observed the opposite phenomenon, the same as Gay-Lussac as observed.

Many others followed these four basic publications of the year 1813. For example, on December 20, 1813, Gay-Lussac read to the Institute a new memoir regarding the combinations of iodine and oxygen (Gay-Lussac, 1813b). The following March 21, Colin and Henri-François Gaultier de Claubry (1792-1851) presented their results on the action between iodine and organic substances (Colin and Gaultier de Claubry, 1814). On June 24, Vauquelin reported his results on the combination of iodine with ammonia, tin, mercury and alcohol (Vauquelin, 1814). Finally, on August 1, appeared Gay-Lussac's extensive memoir (160 pages) (Gay-Lussac, 1814) where he described the general properties of iodine, its combinations with simple bodies, with hydrogen, oxides, and chlorine. He also examined the alkaline and metallic iodides, the iodates, and the ethyl iodide. In this memoir, Gay-Lussac used for the first time, the name hydracids, to name the compounds of this nature formed by hydrogen. Other researches tried to simplify the process of extraction, as well as identify its presence in other natural substances. It was identified in a wide variety of materials, like rocks, oils, marine products, aquatic plants, in the tissue of living animals, in fossils, meteorites, and breathing air.

Nitrogen halides

As we have seen, everyone that worked on the chemistry of iodine prepared nitrogen triiodide, NI_3 ,

and described its explosive nature. This was the second nitrogen halide to be prepared and shown to be explosive. The discovery of nitrogen trichloride (trichloroamine, NCl_3) in October 1811 is probably Pierre Dulong's (1785-1838) most important contribution to chemistry (Dulong, 1813). He was unaware that the product was shock-sensitive and the discovery cost him dearly, he lost a finger during the first experiences and almost lost an eye during the analysis of the product. Dulong prepared nitrogen chloride by reacting chlorine with ammonia. The compound was a new substance that not only had explosive powders; it also had theoretical interest because its synthesis took place with heat storage from the energy released by a parallel reaction. Thus during the action of ammonia on chlorine, nitrogen chloride was formed because of the simultaneous reaction of hydrogen and chloride, a reaction that provided the necessary energy. This stored heat was the energy released during the decomposition of nitrogen chloride, with serious consequences.

Today we know that nitrogen chloride, or trichloroamine, is the only stable pure ammonia halamine. It is a shock-sensitive yellow liquid that boils at 71°C and has a volatility similar to that of chloroform. In the gas phase it can be completely decomposed to nitrogen and chlorine by spark initiation at a concentration of only a few percentage in air.

Similarly, tribromoamine (NBr_3) is a solid that explodes even at -100°C .

Epilogue

As closing remarks it is interesting to mention that Émile Zola used the subject of varec and the production of iodine as part of the central theme in his book *The Zest for Life* (Zola, 1955). The plot takes place at the end of the nineteenth century in the town of Caen, in Normandy, in the northern shores of France. There, the low tides brought into sight the vast stocks of brown seaweed present under the water. One of the main heroes, Lazare Chanteau, decides to invest most of his fortune on the manufacture of byproducts from varech soda, using the low temperature fractional process developed by Herbelin. The business fails and Chanteau sells his part to his partner Boutigny. The latter resumed the low-temperature treatment of seaweed ash and thanks to his cautious persistence, practical sense, and the help of a chemist; he solved the manufacturing problems and became very successful. On hearing this "muttered Lazare dully: every time science takes one step

forward it's because some fool has given it a shove without meaning to." ■

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