

## RESEÑA BIOGRAFICA

# Antoine-Jerôme Balard. The discoverer of bromine

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**RESUMEN.** A Antoine-Jerôme Balard (1802-1876) le debemos el descubrimiento del bromo, ácido oxámico, ácido hipocloroso y el monóxido de cloro, y el haber sido el mentor de Pasteur y Berthelot. El proceso que desarrolló para preparar bromo en cantidad es el mismo que se utiliza hoy día para la producción industrial de este elemento.

**ABSTRACT.** To Antoine-Jerôme Balard (1802-1876) we owe the discovery of bromine, oxamic acid, hypochlorous acid, and chlorine monoxide, and of having been the mentor of Pasteur and Berthelot. The process that he developed for the production large quantities of bromine is basically the same that is nowadays used in the industrial manufacture of the element.

## LIFE AND CAREER

Antoine-Jerôme Balard was born in Figueirolles, Montpellier, on September 30, 1802, into a family of modest means; his parents were winegrowers of poor means. He spent his first years with his parents and was then put under the care of his godmother M<sup>me</sup> Vincent, who promptly noticed the intelligence of the child and saw that he be given the proper education by registering him at the *lycée* in Montpellier. His godmother was not wealthy and Balard grew up under austere economical means that would shape his character.

In 1819, upon his graduation from the Lycée, the social relations of his godmother obtained him an apprenticeship under the guidance of master apothecary Laugier, who owned a pharmacy in Montpellier. At that time apprenticeship in pharmacy lasted six years. The pharmaceutical industry was then non-existent; the master apothecary purchased his raw materials (drugs) and transformed them into medicines following the prescriptions of the

*Codex Medicamentarius*. This Codex, written in Latin, was a voluminous compendium of the official prescriptions, giving careful detailed instructions of the precautions to be taken in the preparation of medicaments, the way they operated, as well as the characteristics and properties they had to have in order to be allowed to be sold.<sup>1</sup> According to Jean Baptiste André Dumas (1800-1884)<sup>2</sup>, at that time pharmaceutical operations constituted the best school for a serious-minded and sharp spirit. They occupied of the production of primary materials from minerals, plants, and animals, learned to observe the results of their reciprocal action, to take into account the influence of air, heat and solvents, and to put all these factors to the best service of humanity.

Balard worked one-and-a half year under Laugier and then two-and-a half year under Blanc, another master apothecary. Balard showed such a gift for chemistry that in 1820, at the age of 18, Laugier authorized him to become *préparateur* of

chemistry to Joseph Anglada (1775-1833) at the *Faculté des Sciences* in Montpellier. A few months later he was appointed *préparateur* at the *École de Pharmacie* in Montpellier, where he took the courses in chemistry and physics given at the *Faculté de Médecine* by Jacques-Étienne Bérard (1789-1869), who permitted Balard to do research at the chemical factory *Fabrique de Produits Chimiques* in Lapaille, of which Bérard was the director. The Parliament of Languedoc had established this chemical factory; its first director was Jean-Antoine Chaptal (1756-1832), who was then replaced by Bérard. It should also be mentioned that Bérard was a former student of Amédée-Barthélemy Berthollet (1748-1822).

When Balard completed four years of his apprenticeship he did not have the legal age of 25 to be admitted as a pharmacist, nevertheless, his masters (Laugier and Blanc) were so impressed by his innate abilities that they recommended that he be dispensed of this requirement and allowed to take the pertinent examinations. In 1825 he took his first two oral exams and registered for the experimental one. On July 5, 1826, he defended his degree thesis "*Essai sur le cyanogène et quelques-unes de ses combinaisons*" (Essay on cyanogen and some of its combinations), which he passed and became qualified as "*pharmacien de 1<sup>er</sup> class*" (pharmacist of the first class).<sup>1</sup>

It was in this period, about 1825, that Balard made his discovery of bromine.

Shortly before, in 1811, Bernard Courtois (1777-1838) had discovered iodine in the ashes of different maritime algae collected from the Ocean and this discovery had had a notable repercussion after Gay-Lussac studied the properties of the new element and showed that it should be classified next to chlorine [isolated by Carl Wilhelm Scheele (1742-1786) from sea salt].<sup>3</sup> Balard decided to investigate if algae collected from the Mediterranean Sea also contained iodine, his results indicated that this was so and that the element was also present in polypods and mollusks. During this work he also made an additional interesting observation: "I have observed that after treating with aqueous chlorine solutions of the cinders of *Fucus* (an algae that contains iodine), addition of starch not only gives place to the blue color zone indicating the presence of iodine, under it appears another zone of intense yellow color. I have also observed this same yellow-orange color when treating the mother liquid of our bitters. The tint is more intense the more concentrated the liquid is. The appearance of this hue is always accompanied by a particular odor."<sup>4</sup>

Balard proceeded to separate the source of the color and study its properties. His results led him to believe that he had discovered a new element, which on the advice of Anglada he named, on first instance, *muride* (from the Latin *Muria*, brine; in Greek, *almuris*, *almuridos*) because it reflected its origin besides being euphonic.

Balard's results were presented to the *Académie des Sciences* by Bérard, as a memoir entitled "*Sur une substance particulière contenue dans l'eau de la mer*" (About a particular substance present in sea water).<sup>4,5</sup> The impression made by his findings was considerable. Dumas, the permanent secretary of the *Académie*, passed among the members a vial containing *muride* (bromine), and commented that the new element had been discovered in the provinces by a young student of pharmacy not by an act of hazard but as the legitimate fruit of scientific research. Balard's memoir was published in the *Recueil des Savants Étrangers* (published by the *Académie des Sciences* for communications from non-members) and fully reproduced in the *Annales de Chimie et Physique*.<sup>4</sup> The memoir presented to the *Académie* had 13 parts and constituted a chemical and physical

study of the element. It described the procedure for extracting bromine from seawater, the physical properties of the element, of hydromuridic acid (HBr), its salts, the reactions with chlorine, iodine, phosphorus, sulfur, carbon, and certain organic substances. In this memoir the name *muride* was changed to *brome*, as suggested by Joseph-Louis Gay-Lussac (1778-1850) (see below).

The fame of Balard was high; he was awarded a medal by the Royal Society of London and he was appointed professor of chemistry at the Lycée in Montpellier. In 1829, only three years after he had received his pharmacy degree, he was appointed adjoint professor at the *École de Pharmacie* and then professor of chemistry at the *Faculté des Sciences*, where he succeeded Anglada. In 1837 he became full professor at the *École*, with a especial Chair in Physics being established for him. The Chair was probably the result of two memoirs that Balard had published on the physical and chemical properties of the rays that constitute solar light<sup>6</sup> and on the properties of the different rays that are separated from sunlight by a prism.<sup>7</sup> In these works he concluded that the maximum heating capacity was at the extreme red while the maximum chemical power was at the ultraviolet.

In 1841 he was invited to join the Sorbonne to take over the Chair in Chemistry that had been vacated by Louis-Jacques Thénard (1777-1857). In 1851 he assumed the chair of Théophile-Jules Pelouze (1807-1867) at the *Collège de France*. For the last position, Balard's chief competitor was Auguste Laurent (1807-1853). On November 11, 1844, Balard was elected to the *Académie des Sciences*. He obtained 28 votes against 26 received by Edmé Fremy (1814-1894). Balard was also General Inspector of Higher Education and a member of the Committee of Public Instruction.

At the first centenary of the discovery of bromine a *Journées Médicales* (medical conference) was held at the *École de Pharmacie*. On that occasion the Municipality of Montpellier unveiled a marble plaque carrying the inscription:

Au Montpelliérain Antoine-  
Jerôme Balard – 1802-1876.  
Découverte du Brome – 1826.

The austere education received from his godmother became Ba-

lard's way of life even at the peak of his career, as described by Dumas and Charles-Adolphe Würtz (1817-1884):<sup>2,8</sup> Balard preferred simple apparatus and homemade reagents to elaborate techniques and materials. He was amiable and generous both to his colleagues and to his students, and took particular interest in the career of the latter, particularly those of Louis Pasteur (1822-1895) and Marcelin Berthelot (1827-1907). Pasteur and Berthelot were assigned as his assistants, in 1846 and 1851 respectively, at Balard's particular request. Balard's papers defending Pasteur's in the spontaneous-generation controversy are well known.<sup>9-13</sup>

Balard had three sons, which unfortunately passed away during his last years, as did his wife. He died on March 30, 1876, at the age of 76. While seriously ill he requested that no speeches be given at the cemetery. The speech that Würtz was to pronounce was published later in the *Journal de Pharmacie*.<sup>8</sup>

The discovery of bromine constitutes the departing point between two epochs of chemistry.<sup>2</sup> Before, the elements were considered independent entities, with no relations among them. Now it was seen that they arranged themselves in natural families and in those families that were incomplete it was possible to predict not only the existence of the unknown elements but also their properties. These first findings would eventually materialize in 1869 with the publication of the Periodic Table of the Elements by Dmitri Ivanovich Mendeleev (1834-1907).

Bromine, like chlorine and iodine was found to be an element present everywhere, in certain silver mines, in plants and maritime animals, in the waters of the ocean, in the Dead Sea and numerous mineral waters; its presence was used to explain the curative properties of the same.

Dumas asked<sup>2</sup>: what is the benefit of having discovered bromine? Shortly after its discovery two different fields of chemistry found it to be indispensable for their chores: (a) The art of image fixation by the chemical action of light was based on the alteration light produced on certain combinations containing silver. Chlorine, bromine, and iodine formed with silver white compounds that were colored by the action of light. A compound of silver and chlorine yielded a black color that the physician Jacques Alexandre César

Charles (1746-1823) had used for reproducing the gross silhouette of objects. Using silver iodide Jacques Daguerre (1787-1851) succeeded in fixing images using a camera, images that the public considered as astounding scientific marvel. Use of silver chloride required that the objects to be reproduced be exposed to the sun for several hours; silver iodide many minutes. With silver bromide the process took place in fraction of a second. It was thus possible to obtain instant images of the passage of a heavenly body, a galloping horse, Venus penetrating the disk of Apollon, the fugitive expression of a face, or a rapid light play.

(b) The second application was in the area of organic analysis and synthesis. Up to that time chemical analysis were usually done by combustion, generating water, tar, combustible gases, and a solid residue of charcoal or coke. The new derivatives of bromine would make these tasks much easier.

#### FIRST WORKS ON THE PROPERTIES AND CHEMISTRY OF IODINE AND BROMINE

As mentioned before, Balard arrived at bromine through his research about the presence of iodine in species living in the Mediterranean Sea and observations about the composition of marsh brines. Already as a *préparateur* at the *Faculté des Sciences* of the University of Montpellier he had published a paper discussing the analysis of iodine.<sup>14</sup> In it he reported that although the discovery of Jean-Jacques Colin (1784-1865) and Henri-François Gaultier de Claubry (1792-1851)<sup>15</sup> about the coloration of starch by iodine provided an extremely sensitive detection method, it could well lead to negative results if the solution contained components that generated hydrogen (today we would say: if the solution contained oxidation agents). Their presence would lead to the transformation of free iodine to hydrogen iodide that did not color starch blue. Balard suggested that the detection procedure include the careful addition of an aqueous solution of chlorine. The latter was lighter than the solution being tested and thus floated on top of it. The typical blue shade would appear at the interface. If the original solution was not clear enough then gentle agitation would increase the thickness of the interface and allow an easier observation. According to Balard, this simple step permit-

ted detecting iodine in compounds where it was present in minute amounts.

Shortly thereafter Balard published his paper about the discovery of bromine that led him to fame.<sup>4</sup> In the opening statement he reported that he had found that addition of aqueous chlorine to the lye of ashes of Fucus (an algae used to produce iodine) containing starch, resulted not only in the formation of a blue-colored zone but also, under it, of another zone tinted strong yellow. This yellow-orange color layer also appeared when the mother liquors of bitterns were treated with aqueous chlorine. In the latter case the formation of color was accompanied by the generation of a strong and particular odor.

In addition, he had noticed the following facts:

(a) The mother liquors treated with chlorine lost their characteristic color and odor after two days in contact with air. Further treatment with chlorine did not regenerate the color and odor,

(b) Addition of alkalis or alkaline bicarbonates also led to disappearance of the color and odor,

(c) The same result was obtained adding a compound that released hydrogen. Materials in this category were sulfurous acid, ammonia, hydrogen sulfide, and particularly zinc in the presence of sulfuric acid.

In the two last cases, addition of chlorine restored the original color and odor.

Balard concluded that the above observations had two possible meanings: (1) The yellow matter was a combination of chlorine with one of the materials present in the mother liquor or, (2) chlorine had displaced the substance from one of its combinations. To decide between these he distilled the resulting liquid and found that the new substance appeared exclusively in the distillate. The distillation residue had none of the properties listed above. He tested the possibility that the new substance was iodine chloride but rejected it after finding that it did not color starch and that all the salts it generated also tested negative for iodine.

The new substance did not decompose under the action of a voltaic pile, even at high temperatures. All these results led him to believe that he had found a new simple body (in modern terms: an element) that was very similar to chlorine and io-

dine in that it produced analog derivatives, although it had strong different traits.

Balard consulted with Anglada who suggested that that the new substance be named *brome*, taken from the Greek *brumz*, meaning bad odor (this statement by Balard conflicts with the report prepared to the *Académie* by Gay-Lussac, see below).

He now prepared a large amount of bromine by treating the saline first with chlorine and then adding ether. The ether layer contained essentially all the bromine. Treatment with an alkaline substance, particularly potassium hydroxide, resulted in the total loss of color and of the penetrating odor. Upon evaporation the resulting salt yielded cubic crystals soluble in water. Bromine was then prepared from the salt by heating it in the presence of  $MnO_2$  and sulfuric acid, followed by distillation and drying with calcium chloride.

Pure distilled bromine had a very intense and disagreeable odor, similar to that of chlorine oxides. It attacked organic matter such as wood and cork and colored yellow the skin yellow. It was also a powerful poison for animals; a drop in the beak of a bird was enough to kill it. It had a density of 2.966, boiled at 47 °C and it did not freeze even when cooled to -18 °C. It dissolved well in water, alcohol, and particularly in ether. It had a very low solubility in sulfuric acid and dissolved very slowly in olive oil. The low solubility in sulfuric acid permitted storing bromine under this acid.

Bromine did not sustain combustion. Heating it alone or in the presence of steam, air, oxygen, hydrogen, or carbon did not affect it, even when in the presence of strong sun light or when passing through a tube heated red. Nevertheless, exposition of a mixture of bromine and hydrogen to a flame or to a burning iron strip resulted in partial reaction. The resulting gas was found to contain hydrogen bromide, a colorless acid gas that dissolved easily in water and aqueous potassium hydroxide. The water solution was very acid. In contact with air, hydrogen bromide acid produced a white vapor, heavier than air that had a piquant smell that made one cough. It did not decompose when passed through a red-hot tube alone or mixed with oxygen, and did not support combustion.

Hydrogen iodide, hydrogen sulfide, and phosphine were promptly decomposed by bromine, yielding hydrogen bromide acid and precipitating iodine, sulfur, or phosphorus, respectively. These reactions were highly exothermic.

Bromine did not decompose water as chlorine did. Hydrogen bromide was decomposed by chlorine generating a brilliant cloud of bromine and some drops of the same. All these results indicated that the composition of hydrogen bromide was similar to that of hydrogen chloride and hydrogen iodide. Metals like zinc, tin, and iron reacted with hydrogen bromide generating hydrogen. Metal oxides reacted in different manners, most of them, like alkalis, earths, and iron oxides, formed liquid combinations that could be considered as hydrobromates. In other cases, such as  $Pb_2O$  and  $Ag_2O$ , the reaction yielded a bromide and water. Highly oxidized oxides did not react with hydrogen bromide or they did not form the bromide corresponding to their high degree of oxidation. They lost part of their oxygen, which decomposed hydrogen bromide and generated bromine.

Balard compared the action of different substances upon chlorine, bromine and iodine, to illustrate their similarities and differences, and to conclude that the properties of hydrogen bromide were intermediate between those of hydrogen chloride and hydrogen iodide. He prepared and determined the properties of the bromides of potassium, ammonia, barium, lead, tin, silver, platinum, and others. He also studied the reaction between bromine and metal oxides (such as potassium, sodium, barium, calcium, magnesium, zirconium, and zinc) and with chlorine, iodine, phosphorus, sulfur and carbon. For example, bromine reacted with chlorine at room temperature producing a yellow red liquid that a strong odor and was a lachrymator. Bromide chloride was very volatile, very soluble in water, and gave place to the combustion of metals forming probably their chlorides and bromides. When dissolved in water sodium chloride, potassium chloride, and barite it generated the chlorates and bromates of the element. This behavior

was similar to that of iodine chloride, a fact that proved that chlorine had more affinity for hydrogen and bromine. On the other hand, iodine was capable of forming with bromine different compounds. Depending on the proportions in which they were mixed the resulting product was either a solid or a liquid. Iodine bromide was soluble in water; the solution reacted with alkalis producing hydrobromates and iodides. Balard prepared also some derivatives bromo derivatives of methane.

Other reactions studied related to the reaction of bromine with organic substances such as vegetable oils, anis, turpentine, and camphor. Balard made the particular observation that highly colored organic substances lost most of their color, and ended yellow, similar to what happened when exposed to chlorine.

Balard concluded his paper indicating the presence of bromine in seawater and bitters marine plants and animals, certain mineral waters obtained from the Pyrenees.

Balard's paper was followed by a report prepared by a committee appointed by the *Académie des Sciences* to verify Balard's claim to have discovered another substance similar to iodine and chlorine.<sup>16</sup> The commission appointed by the *Académie* [Louis-Nicolas Vauquelin (1763-1829), Gay-Lussac, and Thénard], verified the claims Balard's claims as well as his experimental results favorably and suggested, however, that the new element should be called *brome* (bromine) from the Greek word *bromos* (bad smell) rather than *muride*, which was Balard's name for it.<sup>5</sup> The atomic weight of the new element was 9,328, taking oxygen as 1.

The committee ended his report indicating that the discovery of bromine was a very important contribution to chemistry and put Balard in a very honorable place in the advancement of science. They recommended that the *Académie* support his efforts and that Balard's memoir be published in the journal *Recueil des Savants Étrangers*.

## OTHER CHEMISTRY WORKS

### (1) Bleaching

Balard wrote a very extensive paper on the nature of bleaching compounds of chlorine.<sup>17</sup> He first he

traced the history of the bleaching process, from the moment that Berthollet had described its action on colored fabrics. Originally bleaching was performed with chlorine gas or its aqueous solutions, the harmful action it had on the health of workers and in excessive weakening of the cloth prompted the search for alternatives. Berthollet had found that chlorine could be absorbed by a solution of potassium hydroxide and that addition of calcium oxide, or the carbonates of calcium or magnesium to the aqueous chlorine solution, eliminated the health problem without affecting the bleaching properties. Eventually these discoveries led, in 1789, to the manufacture of a bleaching liquid called *eau de Javelle* (the name came from the region near the Seine where the laundries were located). Later on, in 1799, George Tennant of Glasgow found that by using chlorine and slaked lime it was possible to produce a solid bleaching agent. The development of a solid *bleaching powder* was of great importance since it could be transported easily. In addition, Antoine Germain Labarraque (1777-1856) found in 1822 that the bleaching powder had also disinfecting properties (a result of practical importance in dealing with the cholera epidemic of 1832; see Note 1)<sup>18</sup> and increased substantially the market of the product.

Much effort had been put to identify the chemical structure of the active substance (s), its elementary and immediate analysis were well known, but not the chemical structure in which its three components (calcium, chlorine and oxygen) were combined. Two hypotheses were prevalent: (a) the material was an oxychloride where the chlorine added in a weak manner to the metal oxides and (b), that chlorine had reacted with the metal oxides yielding a mixture of different chlorides and a salt that contained a chlorine acid, less oxygenated than chloric acid, and called *acide chloreux* (chlorous acid,  $HClO_2$ ).

In order to clarify this point, Balard made numerous experiments to prepare and separate chlorous acid. Eventually he arrived at a procedure based on bubbling chlorine through an aqueous suspension of silver oxide; part of the silver oxide

## Notes

1. Sadi Carnot (Second Law of Thermodynamics) is usually reported as having died as a consequence of this cholera plague, although this is not true [Wisniak, 2000].<sup>18</sup>

yielded a white compound (silver chloride) and the other a black precipitate (silver peroxide). The reaction was highly exothermic but without release of oxygen. The supernatant limpid liquid had strong bleaching power but after sometime it became turbid, lost its bleaching power, and precipitated silver chloride. The remaining liquid was analyzed and shown to contain silver chlorate. From these results Balard inferred that the original liquid contained silver chlorite that was unstable and decomposed into silver chloride and chlorate. Balard then found that if chlorine continued to be bubbled through the liquid, while heating under vacuum, it was possible to obtain a distillate that contained a very dilute solution of chlorous acid. In order to obtain larger amounts the acid he replaced silver oxide by mercuric red oxide (HgO).

Balard proceeded then to study the properties of pure chlorous acids and its aqueous solutions and found that both had very similar physical and chemical properties. He reported that in both forms it had a slight yellow color and a strong odor, different from that of chlorine and chlorine dioxide. It attacked the epidermis very actively and strongly than nitric acid. It decomposed easily, particularly when heated or under the influence of strong light, releasing chlorine and chloric acid. The acid was not decomposed by chlorine but it was by bromine and iodine. The latter reaction was exothermic, releasing chlorine and producing either bromic acid or iodine chloride.

Similar reactions were observed with sulfur, selenium, phosphorus, and arsenic; Chlorine was released and the pertinent acids formed (sulfuric, selenic, phosphoric, and arsenic), a fact that indicated that the acid was a strong oxidation agent.

Balard studied and also reported the reaction between the acid and metals (such potassium, iron, tin, zinc, antimony, bismuth, and lead) and compounds such as ammonia, cyanogen, carbon disulfide, phosphorus sulfide, phosphine, hydrogen sulfide, and others.

Analysis of chlorous acid in gas form indicated that it had the composition  $\text{Cl}_2\text{O}$  (chlorine monoxide), a composition that was confirmed by many reactions. In other words, it was actually an oxide of chlorine. It also followed that the aqueous solu-

tions corresponded to a compound having composition equivalent that of hyposulfurous and hypophosphorus acids, that is,  $\text{HClO}$ . Balard proposed naming this acid *hypochlorous acid* and its salts *hypochlorites* and reserving the previous name chlorous acid to an acid yet to be found and having the formula  $\text{HClO}_2$ .

Balard also prepared and studied the properties of a large number of hypochlorites (such as zinc, copper, iron, magnesium, etc.).

### (2) *Decomposition of ammonium oxalate*

Balard devoted some of his research efforts to study the action of heat on ammonium oxalate that led him to demonstrate the existence of acid amides. In a paper on the subject<sup>19</sup> he reported that when heating crystallized ammonium oxalate the first stage was an aqueous fusion in the water of crystallization, followed by loss of water and decomposition at about 220 to 230 °C. The gases released were CO and  $\text{CO}_2$ , together with the production of formic acid and oxamide (oxalic acid diamide). More heating generated ammonium carbonate and ammonium cyanide. Eventually, crystals were produced of a new substance that Balard named *oxamic acid* (today: oxalic acid monoamide). He separated the acid by precipitating it with barite. Treatment of barium oxamate with alkali released ammonia, treatment with concentrated sulfuric acid yielded CO and  $\text{CO}_2$ . Boiling an aqueous solution of oxamic reduced it back to ammonium oxalate. From the analysis, Balard concluded that oxamic acid had the global composition  $\text{C}_4\text{O}_5\text{H}_4\text{N}_2$  and that its behavior was similar to that of oxaluric acid, prepared by the reaction between oxalic acid and urea.

### (3) *Amyl alcohol*

France was well known for the wines it produced and several manufacturers had approached Balard with the request to find the reason why certain types of marc brandy (aguardiente de orujo) had a bad taste. The oil of marc had been studied by several scientists and was supposed to be composed entirely by enanthic ether (methyl heptanoate), but the samples that were provided to Balard were of more complex nature; they had been described by Dumas as potato oil (because it origi-

nated by the fermentation of the potato starch), and later as amyl alcohol by Auguste Cahours (1813-1891). Balard confirmed Cahours' findings and proceeded to study the properties of the alcohol and prepare a large variety of derivatives.<sup>20</sup> The alcohol was insoluble in water as were many of its derivatives. Balard reported the composition and method of preparation of fourteen derivatives of amyl alcohol, for example, amyl ether, amyl mercaptan, potassium xanthamylate, amylene (pentyne), amyl valeric ether, and amyl oxalate.

### (4) *Extraction of sodium and potassium sulfates from seawater*

Around 1824, while walking next to the shore of a salt marsh, Balard observed a deposit of sodium sulfate that the cool of the night had made crystallize in a basin where the mother liquors of common salt were kept. He immediately realized the possibility of exploiting these seawaters for the production of sulfate. While experimenting on the subject he noticed a certain coloration that appeared when the waters were treated with certain reagents. The pursuit of this observation and his work on the iodine content of Mediterranean algae, led him to the discovery of bromine.

In the south of France and in the Midi about 200 acres of land were devoted to evaporate by solar evaporation seawater and bitterns for the production of about 20 000 t of common salt per year. The mother liquors left after the crystallization of common salt were usually returned to the sea as worthless. According to Balard<sup>21</sup> this production corresponded to the evaporation of about 800 000  $\text{m}^3$  of water per year and he believed it was possible to obtain about 3 000 t of magnesium sulfate per year from the residual brine. If this amount of magnesium sulfate could be converted into sodium sulfate it would represent a tremendous economic resource because the latter was worth fifteen times more than common salt. This was true even when considering that during evaporation part of the sulfate would precipitate as calcium sulfate. Cooling of the brine to below 0 °C resulted in the crystallization of only minute amounts of sodium sulfate; for this reason Balard recommended making use of the process of double decomposition. Magnesium chloride influenced the solubility of sodium chloride because they were both

chlorides and also that of magnesium sulfate because they were both magnesium salts. On the other hand, it favored the solubility of sodium sulfate by the phenomenon of double decomposition. In addition, sodium chloride would diminish the solubility of sodium sulfate. The practical result of these observations was that in order to produce sodium sulfate it was necessary first to precipitate magnesium sulfate and magnesium chloride together, eliminate the magnesium chloride and then add an excess of common salt. The procedure involved using the hot summer months to concentrate the salts and the cold nights of winter to effect the successive crystallizations. Balard's laboratory results indicated that this procedure was potentially possible and that it yielded hydrated sodium sulfate of very high purity and free of magnesium sulfate. According to his calculations the losses in the different stages of the process would mean that 200 ha of pond would yield 600 t of sodium sulfate instead of the theoretical 3 000. In other words, a pond area of 20 000 ha would be sufficient to provide the annual French needs of sulfate. Balard was convinced after improvement of his process would bring the actual area to less than 6 000 ha.

In modern terms, we can see that in an indirect manner, Balard was anticipating the phase diagram of the complex salt system present.

According to Balard the mother liquors could also be used to supply the potassium salts required by the French industry. At that time potassium needs were supplied by burning wood, of which Russia and America were the main providers. Both countries were becoming more and more reluctant to the burning

of wood and it was possible to foresee the day when potassium would become scarce. On the other hands, potassium was available in huge quantities in seawater; part of it was already utilized by burning marine algae.

Again, solar concentration of the brines present in the 200 ha of ponds would allowed crystallization of 200 t/year (representing 90 t of dry potassium sulfate) of the double sulfate of potassium and magnesium containing six molecules of water ( $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ ). An area of 6 000 ha of solar ponds would suffice for providing all the French needs of potassium.

Balard dedicated himself for 20 years to develop a process for the recovery of sodium and potassium, which were necessary for the manufacture of glass, soap, bleaching and degreasing of textiles. In 1840 he took a patent on his process for the extraction of potassium salts from the mother liquor of salt marshes that had already deposited sodium sulfate under the influence of cold. His many efforts he made to bring his patent into industrial were not successful. In 1850 two events took place that modified fundamentally the market situation, putting sodium and potassium from sea origin in front of considerable competition. Nicolas Le Blanc (1742-1806) had succeeded in producing sodium carbonate by treating sea salt with sulfuric acid obtained from sulfur coming from Sicily. Afterwards, another manufacturer succeeded in manufacturing the acid from pyrites, available in many countries, bringing down substantially the price of sodium sulfate, that Balard's hoped to manufacture it cheaply. The other blow was the discovery in Statssfurt, near Magdeburg, Germany, of natu-

ral deposits of sodium and potassium sulfates. These deposits were so vast that they could supply the world demand for many centuries, at half the market price.

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**RESULTADOS CIENTIFICOS DESTACADOS**  
**MINISTERIO DE EDUCACION SUPERIOR DE CUBA**

## **SENSORES PARA EL CONTROL DE LA CONTAMINACION POR METALES PESADOS DEL MEDIO AMBIENTE**

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*La detección de pequeñas concentraciones de cationes de metales pesados en las aguas residuales industriales, ríos y reservorios acuosos en general, es un problema de gran importancia y actualidad. La complejidad radica no solo en reconocer y cuantificar la presencia de determinado catión, sino de hacerlo selectivamente sin que otros puedan interferir en la determinación. Se dispone de cinco nuevos sensores potenciométricos: dos de Pb(II), uno de Cd(II) y dos de Hg(II) y para determinar aniones de importancia ambiental como el nitrato. En las determinaciones se emplean sales cuaternarias de amonio. El resultado recibió premio nacional de la Academia de Ciencias de Cuba.*