

# PIERRE BAYEN

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**RESUMEN.** Pierre Bayen (1725-1798), un farmacéutico francés, organizador de la farmacia militar, hizo importantes contribuciones a química, la metalurgia y la geología. Dentro de los muchos cargos que ejerció, el más importante fue ser jefe de los servicios farmacéuticos del ejército. Su trabajo sobre aguas minerales lo llevó a descubrir el efecto fulminante de las mezclas de azufre con óxidos de mercurio, que el óxido rojo de mercurio era auto reducible, que durante su reducción se separaba un fluido elástico (oxígeno, que no identificó), y que la oxidación de los metales estos absorbían un fluido elástico de la atmósfera. Estos resultados lo llevaron a ser el primer científico europeo que rechazó la teoría del flogisto (todo esto, años antes que Lavoisier). Junto con Venel rechazaron las afirmaciones que el estaño contiene cantidades venenosas de arsénico.

**ABSTRACT.** Pierre Bayen (1725-1798), a French pharmacist, made significant contributions to chemistry, metallurgy, and geology. Among the many position he occupied, the most important was being head of the pharmaceutical services of the army, His work about mineral waters, led him to discover the fulminant effect of mixtures of sulfur with mercury oxides, that the red oxide of mercury was self-reducing, that during its reduction an elastic fluid separate (oxygen, which he did not identify), and that during the oxidation of metals, they absorbed an elastic fluid from the atmosphere. These results led him to be the first European scientist to openly reject the phlogiston theory (all this, years before Lavoisier). Together with Venel they disproved the claim that tin contained poisonous amounts of arsenic.

## INTRODUCCIÓN

### Life and career<sup>1-4</sup>

Pierre Bayen, born on February 7, 1725, at Châlons-sur-Marne, was the youngest of the seven children of Pierre Bayen (?-1741), a bread maker, and Françoise Legentil (?-1737). His parents died when he was very young and his eldest sister, Anne (1710-?), took care of the family and taught Pierre how to read write, and basic arithmetic, and afterwards sent him to the school at Troyes when he was nine years old. Forced to select a profession that would provide him the means to live, his taste for sciences led him to choose pharmacy, and so in 1747 he begun working as an apprentice for Faciot, a highly reputed pharmacist in Reims. Anxious to improve his knowledge of chemistry, he moved to Paris in 1749 and continued his pharmacy studies under the apothecary Charas. The diligence and ability displayed by Bayen attracted the notice of his master, who gave him every opportunity of improvement and entrusted him with the direction of his laboratory. The next stage came when the philanthropist Claude Humbert Pierron de Chamoussel (1717-1772), who had just built a model hospital to treat the ill poor, asked Charas to recommend him a practitioner capable of managing the hospital pharmacy. Charas suggested Bayen for the job. While carrying on this work, Bayen found the time to attend the chemistry course given by Guillaume François Rouelle (1703-1770).

In 1755, thanks to the recommendation of Rouelle, Bayen was appointed chief pharmacist of the French expedition against the British in the island of Minorca. After the fall of Port Mahon (April 22, 1756), Bayen transferred, with the same position, to the Army of Germany, and stayed as such during the Seven Years War (1756-1763). It was during this period that Bayen carried on the organization of the military pharmacy, his most important administrative achievement. After the signature of the peace of 1763, Bayen was appointed chief pharmacist of the Royal Armies and returned to Paris where he carried on his administrative work and chemical research. At that time the Minister of War was interested in the analysis of all the mineral waters of France and asked Rouelle to select the chemists who carry on the project. Rouelle picked Bayen and Gabriel Françoise Venel (1723-1775); eventually Venel abandoned

the project and Bayen was left alone to carry it to a successful ending. This enterprise led to Bayen's first publications.<sup>5,6</sup>

In 1766 Bayen received his pharmacy degree and became a member of the Collège de Pharmacie.<sup>3</sup>

Bayen died in Paris, on February 15, 1798, at the age of 74, after serving for 42 years as Army pharmacist. Antoine Augustin Parmentier (1737-1813) gave his funeral eulogy at the Société de Médecine<sup>7</sup> (Parmentier, 1798).

Bayen received many awards and honors for his contributions to science and military pharmacy. He was a member of the Société de Médecine, Société d'Agriculture de Paris, Collège de Pharmacie and of the Société Philomatique; he also was one of the General Inspectors of the Service de Santé of the Army. He failed in several opportunities in being elected to the Académie des Sciences. Only after the abolition of the same and its substitution by the Institut National de France, he was elected to the top French scientific institution (1795).<sup>4</sup>

Bayen published nothing before the age of 40. His first publication, the analysis of the mineral waters of Luchon, was inserted in the second volume of *Recueil d'Observations de Médecine des Hôpitaux Militaires*, published by François Marie Claude Richard de Hautesierk (1712-1789), First Physician of the Armies, and Inspector of military hospitals (1776).<sup>8</sup> At a certain moment, the funds for this project were diverted to other purposes, and consequently Bayen found himself analyzing the various specimens of minerals, which he had collected in his travels through the Pyrenees. His work about marble resulted in important architectural considerations for their use.<sup>9-13</sup> He showed the presence of magnesium in schists and suggested using their decomposition to manufacture Epsom salt, which was then imported from England. While analyzing the waters of Bagnères-de-Luchon he discovered the fulminant property of the mixture of sulfur with many combinations of mercury, studied the oxides of mercury and observed, on the one hand, that the red oxide was self-reducing, and that the metal increased its weight during oxidation.<sup>14-19</sup> This led him to prepare oxygen (without realizing it) and to be the first European scientist to reject the phlogiston theory, all this done several years ahead of Antoine-Laurent Lavoisier (1743-1794). After Johann Friedrich Henckel (1679-1744) and Andreas Sigmund Marggraf (1709-1782) reported the presence of arsenic in tin, Bayen and Louis Martin Charlard (1734-1798), were charged with verifying these findings and reporting about the safety of using tin for the manufacture of food utensils and in food use. Their results proved that the claims of Henckel and Marggraf were exaggerated; the amounts of arsenic present in tin were low enough to make its use safe.<sup>20</sup>

## SCIENTIFIC CONTRIBUTION

Bayen published very few papers and booklets;<sup>5,20,21</sup> all his journal publications were reproduced in the book *Opuscules Chimiques*.<sup>22</sup>

### Mineral waters

The French government was interested in building a registry of the mineral waters in the country, and determining their composition. Rouelle was asked to choose the chemists to carry on the project, and he selected Bayen and Gabriel François Venel (1723-1775). As mentioned before, personal reasons forced Venel to abandon the project at an early stage, and Bayen had to interrupt it temporarily after being appointed chief pharmacist of the expedition to the Minorca Island. Within this project were examined the new water source found at Passy, and of sources of Bagnères-de-Luchon.<sup>5,6,22</sup> Differently from other water sources known around Passy, which had been previously analyzed, the new one was found to be acid and to contain large amounts of ferric sulfate. The waters were clear and transparent and did not change their color and taste or deposit sediment, when kept in a vessel carelessly closed for a long time. When heated, they became turbid and deposited yellow orange sediment, even before reaching their boiling point. After boiling they turned blackish but did not react with a gallnut solution.<sup>6</sup>

The first in-depth scientific work of Bayen was related to the analysis of the mineral waters of Bagnères-de-Luchon.<sup>5,22</sup> The extensive report (over 200 pages) was divided into four parts. The first part was a detailed description of the valley and the water fountains of Luchon, located in the middle of the Pyrenees. The small village of Bagnères was named after its warm waters baths, known from the Roman times. Bayen noticed that in the grotto, at the places where the water was stagnant, a thin whitish layer covered its surface, which he identified as sulfur. Over burning carbon, it lighted and burned with a bluish flame, releasing the suffocating smell of SO<sub>2</sub>. The surrounding rocks were covered by a white layer, sometimes in the form of fine strings, others as silky gelatinous flakes. The entrance and the interior of the grotto were completely lined up with a thick layer of incrustations and efflorescence that tasted like ferric sulfate and alum. Bayen reported that the temperature of the water was constant at 65°C. The fountain had many sources (Salle, Reine, Nouvelle, White, Cold, etc.); one named *white source*, because of the color of its waters, and another, *cold source*, because its temperature varied between 21.3 to 26.3°C.<sup>5,22</sup>

The second part of the memoir described the different procedures used by Bayen to determine the amount of sulfur present in the waters of Luchon. At their exit from the ground, the waters were clear and limpid, smelling like hepatic sulfur, and repugnant to the taste. Bayen's results indicated that they not only contained a large amount of the element but that at the time the waters came out of the earth, the sulfur was actually in a state of dissolution. This dissolution stopped when the waters met the cold or the white source, or when cooled when exposed to cold air. As soon as the waters reached the baths they became cloudy and milky. The sulfur could also be separated from the water by simple

addition of a few drops of nitric acid. Bayen went on to investigate if this sulfur was the only factor that caused their milky appearance. Examination of the silky flakes, which covered the surrounding rocks, indicated that they were probably sulfur, but when burning, an empyreumatic smoke masked the odor and the color of the flame. Distillation of the material indicated that it was composed of sulfur and a small amount of empyreumatic fatty oil. The latter did not effervesce when treated with alkali and did not redden syrup of violet.<sup>5,22</sup>

Bayen noted that a black mud was formed in places where the waters became stagnant. He considered that these deposits were a result of the decomposition of ferrous schist, quite abundant in the soil that surrounded them, on top of which deposited the gelatinous flakes.

Bayen then studied the action of several reagents on this mineral water, to get a general picture of its components. He noticed that potassium tartrate, sodium hydroxide, acids, boiled milk, syrup of violet, and sublimed mercury, showed no action, but a few drops of mercuric nitrate produce an abundant black precipitate. On the basis of these results, Bayen decided to study in more detail the reaction with mercuric nitrate. He took a mixture of 123 pounds of water taken from all the sources in the Grotto, added enough volume of the solution of mercury nitrate to saturate the waters, and observed that the mercury precipitated rapidly, in a highly divided state. He then separated the water and washed the precipitate with distilled water, followed by drying; the final product weighed 15.10 g. He followed the same procedure for other sources located outside the Grotto (Salle, Reine, nouvelle source, and cold source). All these precipitates when thrown over burning coal (except for the one from the cold source) were seen to burn with a bluish flame and give off a smell of  $\text{SO}_2$ .<sup>5,22</sup>

From all these results, Bayen concluded that the sulfur contained in the water was dissolved in it by means of an intermediate compound, which originated the hepatic smell they had. This smell disappeared after exposing the water to the air for several days. According to Bayen, the sulfur acted on the intermediate, joined to it its acid part, *and the phlogiston that constituted it, dissipated in the air* (as will be seen below, shortly thereafter Bayen rejected the phlogiston theory).<sup>5,22</sup>

The next stage was the examination of the waters of Luchon by distillation and evaporation, as well as the waters left after precipitation with mercuric nitrate. The results indicated that the amount of residue left by one pound of water varied according to the source, from 0.19 grams for the Salle, to 0.06 grams for the cold source. The residue after precipitation varied between 0.084 grams for the waters of the grotto to 0.056 grams to those of the new source.

The third part described the properties and analysis of the evaporation residues of the waters of the cave, which Bayen named fixed products. Bayen also discussed the different precipitation processes taking place as well as the white color that the waters contracted in the baths. The results indicated that the waters from the grotto, Reine, and Salle, contained sodium sulfate (Glauber's salt), chloride, and carbonate, and a fatty material, which generated an empyreumatic odor; the cold source also contained a calcareous chloride. The insoluble pellicular material that accumulated on the surface of the waters during their evaporation was shown to be an earthen substance, capable of vitrification. The results of the many exams carried on proved that the Luchon waters contained sodium sulfate, sulfide, and chloride, alkali material, and a small amount of fatty material and vitrifiable earth, not attacked by acids. The fatty material, which Bayen assumed to be bituminous, burned easily leaving a carbonaceous residue.<sup>5,22</sup>

Bayen used the same procedures to analyze the residue of the waters left after being treated with mercuric nitrate and filtrated. He reported that in spite of the care he had taken in performing the corresponding tests, he had been unable to detect the presence of sodium chloride, or sulfate, as well as alkaline material.

Bayen had assumed that the characteristics of the mercury precipitated, was the best proof that the Luchon waters contained sulfur. Nevertheless, he decided to carry on a sublimation of the salts in a *closed* vessel, to try to determine the processes and changes that suffered the mercury on precipitating from an aqueous solution of sulfur, alkaline matter, marine salt, and sodium sulfate. The different sublimated products accumulated at progressive sections of the neck of the retort; the one located immediately at the entrance of the neck was a dark purple red scaly material, identified as cinnabar (mercuric sulfide); it was followed by pure mercury and a layer of pure sulfur. The fourth product was a layer of gray pulverulent material, composed of small drops of revived mercury. The solid residue in the retort (caput mortuum) was a black glistening powder, containing a small amount of mercury; exposed to fire it inflamed and detonated easily and strongly.<sup>5,22</sup>

Bayen concluded that the mercury precipitates from the Luchon waters were a mixture of mercury precipitated by an alkali, pure mercury, turbith mineral (mercuric sulfate), sulfur, a vitrifiable earth, and a small amount of bituminous matter.

According to Bayen, the high temperature of the waters, as well as their milky aspect, pointed, on the one hand, to their being in contact with sub terrain fires or volcanoes, and of the other hand, of being the result of mixing two waters loaded with different solutes, and following reactions, which produced new soluble salts, while the sulfur and the earths remained suspended in the liquor, until after a long rest, they reached the bottom and became a sediment. Bayen considered that the artificial mixing of the waters from the cold source with those of the white one was a mistake because the accompanying chemical reactions diminished their beneficial properties.<sup>5,22</sup> In the fourth and last part, Bayen examined the saline (vitriolic-sulfate) efflorescence found near the mineral sources, the rocks, and the stones covering the ancient Roman baths, as well as the rocky strata over which flowed the white and the cold

sources. Although at first sight, this would imply that the waters contained these materials, the experimental evidence proved that it was not so. The rock bed over which the water traveled was mainly composed of schist, marble, quartz, and micaceous granite. The interstices were filled with schistaceous earth, blue when wet and gray when dry, and tasting and smelling like potassium sulfide; sublimed, it released sulfur. After conducting many experiences on all these components, Bayen concluded as follows: (a) all terrains wetted not by steam but by liquid water, contained sulfur in an extremely divided state, higher than the one that could be achieved in the laboratory by sublimation of precipitation; (b) earths and stones deprived of contact with air and placed in surroundings where they were humidified by mineral waters during a long time, contained sulfur and no salt; these earths, exposed to the air soon became vitriolic-aluminous, by decomposition of the sulfur; (c) the saline efflorescence near a mineral water source, was composed of calcium sulfate, aluminum sulfate, iron sulfate, and also, sometimes, of magnesium sulfate (Seidlitz salt). In general, alum was the dominant component, followed by iron sulfate (sometimes crystallized, sometimes in solution); (d) the thick incrustations accumulating on the walls of buildings or on the baths, were actually gypsum; from which the sulfates of calcium, aluminum, iron, and magnesium, had been removed by washing; (e) the schist which made most of landslides, contained, in addition to iron, alumina and calcium; and (f) the rock schist, from which emerged the cold source and the white source, contained iron, alumina, magnesium, an a little of calcareous earth.<sup>5,22</sup>

The last experiences were devoted to explaining why the rocks surrounding the source of the water sources contained so much sulfate salts. According to Bayen, the Luchon waters, loaded with sulfur, humidified the surrounding terrain, introducing and depositing in its pores schistic rocks, which reacted with the original material transforming it into a pyritic state. Their contact with air led to efflorescence, which accelerated the process of sulfatization, while the material was exposed to a more humid and warm air.<sup>5,22</sup>

### Mercury precipitates

Bayen's papers on the subject are very important because of their relation to the priority of the discovery of oxygen, and rejection of the phlogiston theory. Before describing them, it is appropriate to refresh the basic tenets of the phlogiston theory.<sup>23</sup> This theory was born around 1700 and lasted for about one hundred years. It provided for the first time a unifying approach to widely different chemical and physical phenomena and as such was adopted by the most famous European scientists, particularly the French ones. Its demise came with Lavoisier's new insights into the phenomena of chemical reactions in general and combustion in particular,<sup>24</sup> as well as about the composition of air. The theory originated around 1700 from the ideas and experiences of Joachim Becher (1635-1682) and consolidated with the teachings of George Ernst Stahl (1660-1734).<sup>25</sup> According to Becher, material substances were composed of the three elements, air, water, and earth. The basic tenets were based on the fact that a large number of chemical substances were combustible; some like carbon and sulfur burned with a flame and released a large amount of heat, while others, like the metals, suffered a deep transformation and became calxes. According to Stahl these common features were due to a component, which was present in all bodies and carried the property of combustibility. It was the *inflammable principle*, which Stahl named *phlogiston* (from the Greek  $\phi\lambda\omicron\xi$ , flame).<sup>26</sup> The easier a body burned the more phlogiston it contained. It was also liberated during the calcinations of metals where it constituted a common principle. After combustion there remained a *terre*, or a *chaux* (calx), that was believed to be a simple body.

The differences between the different metals arose from the differences in their calxes (the residue of combustion). During combustion phlogiston was released in the form of fire and dissipated in the air. The flame contained the heat in pure and free forms, while phlogiston constituted combined heat. Hence combustion was simply the transformation of combined fire to free fire. Stahl showed that it was possible to recover from a metallic calx the starting metal by heating it with a body rich in phlogiston, such as carbon.<sup>26</sup>

The initial success of the phlogiston theory was its being the first consistent general theory that tried to explain chemical reactions in general and combustion in particular, as well as being a broad conceptual scheme into which could be fitted most of the chemical phenomena known in the eighteenth century. Nevertheless, the theory had a basic defect: if phlogiston was a natural material (ponderable), its release by combustion should be accompanied by a *decrease* in weight and not by an increase, as actually observed: The resulting body was always heavier than the original one. This result could not be explained even if phlogiston was assumed to be imponderable or to have a *negative weight* (!).<sup>27</sup>

By 1778 Lavoisier had developed his theory that combustion and calcinations depended on the combination of the combustible or metal with oxygen; his hypothesis was opposite to that of Stahl because he did not have to assume the existence of fire in combustibles and metals and by interpreting combustion as a process of combination of a combustible with part of the air. The heat and flame came not from a solid combustible; the source of fire was a fluid (*caloric*). Thus, according to Stahl's theory calcination was an analytical operation because the metal or any other body decomposed into phlogiston and calx, and reduction was a synthetic operation because the calx recovered its phlogiston. In Lavoisier's theory it was exactly the opposite: calcination was a synthesis because the metal absorbed something when it increased in weight; reduction was a decomposition because carbon instead of withdrawing, it

added something to the metal and caused it to reduce its weight, exactly in the same amount it gained during calcinations.<sup>27</sup>

Lavoisier postulated that ordinary air was composed of two very different substances, a pure part, which supported combustion and another part (mephitic air, azote), which did not: "The principle which combines with metals during their calcinations, which increases their weight and constitutes them in the state of a calx, is nothing other than the purest part of air and such that, if the air, after having engaged in a metallic combination, becomes free again, it appears in an eminently breathable state".<sup>27</sup> There still remained other baffling phenomena that the phlogiston theory did not explain well: There were two kinds of inflammable air; Lavoisier distinguished between light inflammable air (hydrogen) and heavy inflammable air (carbon monoxide); its composition was unknown and it yielded fixed air (carbon dioxide) on burning. These results, which could not be explained by Lavoisier's new theory, were easily explained by the phlogiston one. Joseph Priestley (1733-1804), for example, had obtained inflammable air by heating finery cinder (iron oxide, Fe<sub>3</sub>O<sub>4</sub>) with carbon. Since according to Lavoisier, inflammable air was a constituent of water, it could only be produced in the presence of water, hence wrote Priestley, this meant that the new theory negated the presence of water in bodies, it saw in finery cinder an oxide composed only of iron and oxygen and did not admit the presence of water in the carbon that formed at higher temperatures. Contrary to this, the phlogiston theory claimed that finery cinder was impregnated with water that replaced the phlogiston, and water was a constituent of all airs, so much that inflammable air resulted of the union of the water contained in finery cinder with the carbon of the phlogiston.<sup>27</sup>

On August 1, 1774, when heating minium (the red oxide of mercury, HgO) in a closed vessel, Priestley obtained a gas that maintained the flame of a candle. Sometime later, Carl Wilhelm Scheele (1742-1786) also isolated oxygen, but his results were not published until 1777. Scheele and Priestley believed in phlogiston, and for the latter, the gas he had obtained was dephlogisticated air.<sup>2</sup>

Bayen's second, and most important work was named *Essais d'Expériences sur les Précipités Mercuriels, dans la Vue de Découvrir leur Nature*. It was composed of four memoirs published successively in the *Journal de Physique* between February 1774 and December 1775. In the first memoir<sup>14</sup> he quoted his findings about the detonating properties of mercurial calxes, as reported by Richard de Hautesierck in *Recueil d'Observations de Médecine des Hôpitaux Militaires*:<sup>8</sup> «Heating in a glass retort a mixture of sulfur and the precipitate obtained from treating a solution of mercury nitrate with fixed alkali, resulted in an explosion similar to the firing of a rifle...the retort was completely destroyed and its fragments deposited 7 to 8 feet away...When the same experience was conducted in an open vessel, a small amount of fumes were produced, and the material fulminated without brightness...a red black powder was left in the apparatus...This powder, after being washed several times with distilled water, dried, and then heated, sublimated as cinnabar...the same results were obtained when using corrosive sublimate (*sublimé corrosif*, HgCl<sub>2</sub>)".<sup>14</sup>

Bayen found these results very intriguing and decided to study the reaction in more detail. He went on to report the many experiences he had conducted regarding the precipitation of solutions of mercury nitrate (or chloride) with an alkali (potassium carbonate, potassium hydroxide, ammonium chloride, borax, and limewater), and heating the red precipitate with sulfur, in open and closed vessels. In every situation he observed the same phenomena: a strong or weak detonation (depending if the vessel was closed or open), and sublimation of mercury revived, mercury sulfide (cinnabar), and sulfur. The various sublimates were collected in different positions in the neck of the retort. Additional experiments were conducted in the presence of carbon (phlogiston) and in these, Bayen found that all the original precipitate had decomposed and all the mercury revived. He observed that the precipitate obtained with ammonium chloride and heated *without* phlogiston (carbon) revived all of the mercury, while that obtained with fixed alkalis yielded less than half the amount of liquid mercury. Bayen explained the detonation as a consequence of "the movement kindled in the mixture of mercury of sulfur at the moment of combining to form cinnabar".<sup>14</sup>

Bayen begun his second memoir, indicating that the results he had obtained thus far clearly proved that the mercury precipitate deposited from its acid solution by means of an alkali weighed more than the mercury before its dissolution by an acid. A similar increase in weight occurred in the calxes obtained by calcinating a metal in an open vessel. Scientists had also discovered that when reducing a calx to the metal state it experimented a substantial reduction in weight. Bayen was now intent in finding the reason of this increase and decrease in weight. He now announced that he was moving away from the Stahlian principles, "my statements will still be during certain instants, in accord with Stahl's doctrine about phlogiston, but I will substitute them by others as soon as my experiences demand it".<sup>14</sup>

Scientists had used a myriad of reasons to justify the increase in weight that occurred on calcinating metals: Nicolas Lemery (1645-1715) by addition of tiny round igneous particles, Charas by the acid contained in substances that fed fire, Johann Friedrich Meyer (1705-1765) by a substance acid he had named *acidum pingue* (the primitive acid), Joseph Black (1728-1799) by fixed air released by alkalis, etc., etc. According to Bayen, it was clear that all these denominations represented one and the same substance, which he decided to name *elastic fluid* (following Lavoisier's concepts). Bayen reported that in one experiment he had dissolved 4 ounces of mercury in nitric acid and after treating the solution with potassium carbonate he had separated a precipitate weighing 4 ounces and 39 grains These

39 grains (2.2% of the original weight) could, in principle, be due (a) to the adherence of part of the solvent or the potassium salt, or (b) to the fixation of an elastic fluid.<sup>14</sup>

Once again, Bayen carried on a large number of experiments in which he heated the mercuric precipitate in open and closed vessels, with or without carbon, and measured the gaseous and solid fractions obtained. The amount of gas released was expressed as the weight of water displaced in his pneumatic apparatus. Reducing the metallic calxes with carbon resulted in revived mercury and the release of a gas heavier than atmospheric air (fixed air), which during the night became absorbed in the water under the bell. This water acquired a sour taste and dissolved iron filings, as shown by the red violet color it acquired when treated with nutgall powder. The experiences carried on without carbon also revived the mercury, but released a different elastic fluid: it was insoluble in water, lighter than fixed air and heavier than atmospheric air. All these results led Bayen to conclude as follows: (a) the mercury precipitates were self-reducible, (b) carbon was not necessary to revive mercury, (c) the hypotheses that he had previously assumed within the frame of Stahl's theory, were false; (d) the elastic fluid removed from the precipitate was unable to combine with water, while the one obtained by calcination (with carbon) did it promptly, and (e) there were two reasons why the precipitate increased in weight; one was the intimate combination with the solvent (the acid), and the other not the loss of phlogiston but an intimate combination with an elastic fluid, whose weight had added to that of the metal.<sup>14</sup>

In the third memoir, published in February 1775, Bayen reported the results of his experiments on the preparation and increase (or decrease) in weight experienced by the precipitates of four different mercury calxes prepared by either precipitation with alkali, or by calcination. He found that the four calxes, after being cleaned of all foreign material, were basically identical. All released the same amount of elastic fluid, dissolved in different acids without effervescence, their red color was equally intensive, and in all, the mercury had lost its property of alloying with gold. He commented that when mercury was heated in a sand bath, in a flask open to the atmosphere, the metal would raise, attach to the walls of the flask, and lose its fluidity and brilliancy, while converting into a flaky substance, sometimes crystallized, but always red and weighing more than the mercury employed in the operation. In Bayen's words: "To justify the change that this calcination has effected on the bright silver appearance, should we say, according to certain Stahl disciples, that fire has caused the metal to lose one of its constituent principles, the phlogiston, and that to this loss it owes its calx state? No, obviously, this would mean saying something denied by experience; hasn't it been demonstrated that far from losing one of its principles, mercury has acquired a new one, which was combined with another body, and that only from this combination has resulted the metamorphosis observed after calcination? Moreover, how can we conciliate the increase in weight with the loss of one of the constituent principles? A problem that after a long time, Stahl's disciples have created to themselves, without ever being able to solve it. To believe, as some of the chemists of the last century and the present one, that the phenomenon must be attributed to igneous corpuscles having the property of passing through the pores of the glass and attaching themselves to the metals, is really, accepting a specious opinion... The fire of our furnaces cannot convert the metals into calxes without the help of air, but the latter, can do it without the assistance of fire... we must search in air (together with the physician Jean Rey) the reason for the increase in weight experimented by mercury, and all other metals during calcination... Of all the substances known to be present in the atmosphere, which one is the one that calcines metals? Is it the elastic fluid pure and simple, is it the same fluid already combined so as to form an acid genre, or is it one of other fluids foreseen in the air that surrounds us... Since we do not know the fluid that raises from the mercurial calxes at the time of their reduction, but from its properties which will be discovered, I frankly declare that my knowledge about this entity is so narrow that I do not dare speak about its nature".<sup>14</sup>

As stated by Edmée Bouillon-Lagrange (1764-1844): "It is unfortunate that Bayen did not analyze the gas released by when the mercury precipitates were reduced by heat in closed vessels; had he done it, he would have anticipated Priestley in his discovery of oxygen and Lavoisier in the creation of the pneumatic doctrine".<sup>28</sup>

The fourth and last memoir was rather limited in scope: a study of the material called turbith mineral, which Bayen prepared according to standard pharmaceutical practice.<sup>17</sup> He reacted mercury with concentrated sulfuric acid, separated the liquid from the resulting yellow powder, and washed the latter with distilled water. The dry powder, when heated in a retort, produced five different products: (a) SO<sub>2</sub> in sufficient amount to make water very acid and prove that turbith mineral contained sulfuric acid, (b) a remarkable amount of elastic fluid, (c) revived mercury, (d) a white sublimate, and (e) a gray powder, found to be a mixture of the lightest fraction of the white sublimate and pure mercury. No residue was left in the retort.

In a second experiment, Bayen treated the solution resulting from the previous experiment with potassium carbonate, separated, washed, and dried the resulting yellow precipitate, and then heated it in a retort, as previously. Once again, SO<sub>2</sub> was released and the mercury was revived. After repeating these experiments several times, under different conditions, Bayen concluded that (a) in every sublimation turbith mineral lost part of its sulfuric (vitriolic) acid as SO<sub>2</sub>, (b) this loss resulted in the conversion of the mercury into calx, followed by mercury revivification and release of a large amount of the elastic fluid, to which it owed its increase in weight, and (c) sublimation distillation was a reliable procedure for decomposing completely mercury sulfate and the turbith mineral. Bayen came once against the phlogiston theory, which claimed that mercury, on changing into turbith mineral, increased its weight,

hence it had lost phlogiston: the increase in weight was “not due to loss of phlogiston, as has been supposed, but to a new combination of the mercury with another body which the atmosphere furnishes to this mineral when it calcined by itself, or which it takes from the acids when it is calcined by the way of dissolution”.<sup>17</sup>

Before closing, it is of interest to quote the comments of Pierre Labrude about the role of Bayen in the discovery of oxygen and rejection of the phlogiston theory: “Lavoisier was present at the 1774 session of the Académie des Sciences where Bayen presented his results. He followed closely the works of the French and foreign chemists, particularly Priestley. He repeated their experiences and knew how to pull up the understanding elements that he missed and looked for so long. He can be criticized that he did not quote Bayen and did not give him the recognition he deserved... Certain authors have defended Lavoisier saying that he was unaware of the results of Bayen and other chemists... Thus Bayen gave up the phlogiston theory well before other chemists, and incontestable was the first in Europe to do so. This rejection earned him the criticism of Macquer, who in the first edition of his *Dictionnaire de Chimie*<sup>29</sup> wrote “In spite of the sincere respect I have for the talents and beautiful experiences of M. Bayen, I cannot avoid saying that he has rashly sliced out such a significant important subject.” On the other hand, Fourcroy, a defender of Bayen’s priority, wrote:<sup>30</sup> “He needed only to examine the gas released in his experiments... to have outdistanced Priestley in his discovery of vital air (oxygen) and Lavoisier in the creation of the pneumatic theory... Bayen was, together with Scheele, Bergmann, Black, Cavendish, Lavoisier, and Berthollet, one of the creators of the great modern chemical revolution... To Bayen we must credit the first attacks to the phlogiston doctrine and the first proposal of the pneumatic doctrine. Because Bayen had recovered carefully the air released from mercury calxes during their reduction; he had measured the amount and estimated the weight, he had shown that during calcination metals removed from atmospheric air or from acids, that it was not by the loss of a principle, as claimed by the Stahlans, but by the real acquisition of a true aerial principle that the calcination took place. He had foreseen that the same principle of the air that calcined the metals was contained in the acids, and particularly, in those of nitrogen and sulfur. The experiences, which he had conducted, had put him at the head of the antiphlogiston chemists, because he had expressed before Lavoisier...<sup>30b</sup>”

Bayen, on the contrary, recognized the pioneering work of Jean Rey (1583-c1645) in explaining the increase of weight that takes place when converting a metal to its calx. According to Rey, during the heating process the heavier air in the furnace adhered physically to the already formed calx. Bayen sent a letter to the Abbé Jean-Baptiste François Rozier (1734-1793), editor of the *Journal de Physique*, written in the following terms: “The cause of the increased weight that certain metals experience by calcination, has, at all times, been a subject of speculation and research with chemists and natural philosophers (who) endeavored to explain this phenomenon; but amongst them all, we must... distinguish Jean Rey, a physician of Périgord, who lived at the beginning of the last century. His work... appears the more deserving to be rescued from oblivion because the reason which he assigns for the increased weight of the calxes of lead and tin, has an immediate relation with that, which is on the point of being acknowledged by all chemists... After I had published in your journal, the second part of my experiments on the calxes of mercury, that I became acquainted with Rey’s book. I could not mention it in the very short enumeration I then gave of the different opinions on the cause of the increased weight of metallic calxes... I hasten to do justice to an author, who... has succeeded in assigning the true cause of that increase. I hope, Monsieur that you will concur with me, in making known Rey’s excellent work. Your journal is read throughout France, it is spread over foreign countries; if you would insert this notice in it, the chemists of all countries would soon know, that it was a Frenchman, who by the power of his genius and reflections, first guessed the cause of the increased weight that certain metals experience when converted into calxes, by exposure to the action of fire, and that it is precisely the same as that, whose truth has just been proved by the experiments which M. Lavoisier read at the last public sitting of the Académie des Sciences”.<sup>16</sup>

The work on mercury precipitates and his position as military pharmacist, led Bayen to carry on additional work on mercury medicines, particularly, some preparations claimed to cure venereal diseases such as Belet’s syrup,<sup>8</sup> the Keyser droplets, and *Eau des Nègres* (against worm). He also published a paper giving a detailed description of his procedure for preparing fulminant mercury.<sup>19</sup>

### Spathic iron

The first memoir appearing in the second volume of the *Opuscules* described the analysis of a mineral of spathic iron, known in Germany as steel mineral (siderite).<sup>9</sup> According to Bayen this mineral was known by the naturalists under the name *mina ferri alba spathi-formis*; the mineral was a gray soft mass of rhomboidal crystals, aggregated in semi transparent thin strips, sometimes containing quartz or small pyrites, and non-attracting. Exposed to heat, the ore decrepitated strongly, turned black and lost about one third of its weight. Calcined it was strongly attracted by a magnet. After several experiences (by heating) with the chemico-pneumatic apparatus, Bayen concluded that one-ounce of ore released 189 grains of gas, which displaced 216 ounces of water. This meant that one volume of gas was equal to about one ounce of water, or that the density of the gas and the density of liquid water were in the ratio 1:658. Believing that the gas released was fixed air (CO<sub>2</sub>), Bayen tested it with a bird to see if it was harmful. The bird fainted out and revived when exposed to atmospheric acid. All the symptoms showed the gas suffocating and

probably of the same nature as the one present in the Grotto of the Dog in Italy. The gas turned the water sour and gave it an odor similar to phosphorus (*sic*). The next set of experiments studied the action of sulfuric, nitric and hydrochloric acids on the mineral. The ore dissolved almost completely in warm sulfuric acid, with much effervescence, producing a solution of iron sulfate accompanied by a few grains of quartz. No precipitation occurred when a knife was immersed in the solution, proving that no copper was present. Nitric acid produced the same results; evaporation of the solution to dryness left a residue of red brown iron oxide. According to Bayen, these results proved that the ore contained about 2/3 of iron and 1/3 of a volatile substance that evaporated by dissolution in an acid or by calcination in an open or closed vessel. Similar results were obtained with HCl, except that the residue showed some black spots, which led Bayen to believe that the mineral contained zinc. To test this hypothesis, Bayen prepared a mixture of calcined ore with iron sulfate and distilled water, and let it digest for several days, under agitation. After filtration and evaporation to dryness, he found a small amount of crystals of a white sulfate, proving that the ore contained a small quantity of zinc.<sup>9</sup>

The next set of arguments was used for a surprising purpose: to prove that the ore contained the iron in a *metallic form*: (a) The calcined mineral was attracted by a magnet; (b) the ore was easily dissolved, with live effervescence, in nitric acid; (c) the same procedure revived mercury from cinnabar; and (d) exposure to heat, in a closed vessel a mixture of minium and ore, reduced the lead in the same manner that it was when heating a mixture of minium and iron fillings.<sup>9</sup>

Bayen ended his paper with the following conclusions: (1) the spathic ore was a combination of iron in its metallic state, and gas; the latter gave iron the property of crystallizing in the form it was present in the mineral; (2) the iron and the gas were present in the ratio 3:1; (3) the ore contained a small amount of zinc; and (4) in its raw form, the ore contained sometimes, small amounts of quartz and calcareous spar.<sup>9</sup>

This memoir gave place to a scientific debate regarding Bayen's conclusion that the mineral of spathic iron contained zinc, and contained the iron in its metallic state. As was customary, the Académie des Sciences appointed a committee formed by Louis-Jean-Marie Daubenton (1716-1800) and Lavoisier, to evaluate Bayen's memoir. The committee reported (February 21, 1776) that Bayen's memoir was well done, that his experiences had been conducted properly and the appropriate conclusions drawn; consequently they recommended that it should be printed in the *Recueil des Mémoires* presented to the Académie by external scientists.<sup>31</sup> The only significant remark was that in 1769 Balthazar-Georges Sage (1740-1824) had read to the Académie a memoir regarding the analysis of a spathic iron mineral in which he had concluded that the mineral was a combination of iron and hydrochloric acid, insoluble in water due to the presence of a fatty material.<sup>32</sup> One pound of this mineral produced by distillation, 35 pounds of HCl, Bayen, on the contrary, had reported that the mineral of spathic iron did not contain HCl.

Torbern Olof Bergman (1735-1784), at about the same time as Bayen, had analyzed the spathic irons (1774), without finding zinc, and sometimes, finding manganese. He believed that iron was present in the ore in the same degree of oxygenation as ferrous sulfate. Jérôme Dizé (1764-1852) repeated the analysis of the mineral on the same sample used by Bayen and found that it contained zinc. Sage<sup>33</sup> claimed that spathic iron did not contain lime, but contained manganese in the proportions reported by Bergmann. The manganese was obtained as its sulfate in white prismatic tetrahedral crystals, which crystallized before iron sulfate. Hippolyte Victor Collet-Descostils (1773-1815) conducted a very detailed analysis of the different reports, carried on a large number of experiments, and reported that he believed he had "discovered the cause of the different results, which they announced, or the errors, which others had committed".<sup>34</sup> Bayen was correct in assuming that the ore contained a gas of the nature of fixed air, small amounts of quartz, and some times also of calcareous spar. The inference that in the ore the iron was in the true metallic state was so inadmissible that there was no need to discuss it. Sage was wrong in his identification of manganese sulfate on at least three counts: (a) the crystallization form reported by him actually corresponded to that of zinc sulfate; (b) the crystals of manganese sulfate crystallized in another pattern and were slightly red and not white; and (c) manganese sulfate was more soluble in water than ferric sulfate and hence should crystallize *after* it. Collet-Descostils chemical analysis of spathic iron ores from different geographical sources indicated that it contained, by weight, 49 to 50.5% red iron oxide, 1.5 to 10% red manganese oxide; 2 to 12.5% magnesia, 0.3 to 05% lime, 0 to 2% quartz, and 34.5 to 63.3% material to be lost by calcination. He remarked that magnesium sulfate crystallized nearly similar to zinc sulfate, and that this similarity of form had probably led Bayen into his mistake, because he did not examine the crystals he obtained.<sup>34</sup>

## Tin

The last major work of Bayen was his study of tin.<sup>20,22</sup> Around 1740 Johann Friedrich Henckel (1679-1744) had announced that tin contained arsenic, and in 1746 and 1747 the Academy of Sciences of Berlin published two memoirs of Andreas Sigmund Marggraf (1709-1782) reporting that he had repeated Henckel's experiments and obtained the same results. These works raised immediately an alarm because of the extensive use of tin in food utensils. The French government promptly acted and Jean Charles Pierre Lenoir (1732-1807), lieutenant general de police of Paris, ordered the Collège de Pharmacie to investigate the question in detail. A committee formed by Hilaire



Marin Rouelle (1718-1779), Bayen, and Charlard was appointed for this purpose. Rouelle died shortly thereafter and Bayen and Charlard were left to carry on the job.

The monograph they produced was divided in four parts. The first part was an historical introduction describing the ancient literature references mentioning the metal (biblical, prophets, poets, and ancient chemists), the geographical sources of the metal, its use in a wide range of activities (utensils, decorative items, medicines, etc.), and the fact that it had always been considered inoffensive to human health. He then classified and described the three tin types, which were traded in France: (a) pure tin as sold by the foundries, originating from England or the Indies and sold in the varieties known as Banca and Malacca. Bayen named these as pure or primitive tins; (b) tin alloys, also sold by the foundries in the composition required by the different regulations; and (c), the wrought tin used by the community of potters.<sup>20,22</sup>

The first set of experiments was devoted to study the effect of heat on the different primitive tins, using open and closed vessels. In every case Bayen observed the formation of a very small amount of sublimate, which condensed as a white powder. Four ounces of tin (226.8 g) yielded about 0.25 grains (0.016 g) of sublimate. Margraff had also observed the formation of this sublimate and assumed that it was arsenic, noting that the quantity formed was too small to carry on a chemical analysis. Bayen wrote that it was true that the amount of sublimate was certainly very small, but even a smaller quantity put on burning coal was enough to test by the odor of the fumes, if it was arsenic. The result was negative. To further justify his hypothesis, he fed a small dog with various dose of the sublimate, without observing any pernicious result. Bayen believed that this sublimate was nothing but a tin calx, similar to the zinc flowers. In addition, Margraff had also dissolved tin with aqua regia and noted that a white powder residue was left, which he assumed to be arsenic. Bayen carefully repeated, step by step, Margraff's experiments, and analyzed the white residue without detecting the presence of arsenic. Since it was possible that his samples did not contain arsenic, Bayen went one step further and prepared a series of alloys of tin with arsenic in different proportions. For this purpose he heated 7.65 g of arsenic (the name arsenic was commonly used for the trioxide,  $As_2O_3$ , more than for the element) with 178 g of tin in a closed retort and observed that a extremely small quantity (0.12 g) of arsenic sublimated, leaving a metallic button weighing 4 ounces and containing 1/16 of its weight in arsenic. This alloy crystallized in large facets and was more fragile and zinc. Bayen "diluted" this alloy by fusing it with more tin so as to obtain alloys containing 1/32, 1/64, and 1/128 of their weight in arsenic. The most diluted alloy was ductile enough to be worked for pottery uses. When the richest alloy was treated with aqua regia, the tin was completely dissolved while the arsenic deposited as a white powder, which little by little became black. After separating the powder, washing with distilled water and drying, Bayen put it on burning coal and observed that the white fumes generated had the typical smell of arsenic. The same results were observed with all the alloys. Bayen now repeated the dilution procedure and found that treatment with aqua regia allowed discerning the presence of arsenic calx down to a content 1/1024.<sup>20,22</sup>

In the next set of experiments Bayen studied the action of HCl, nitric acid, sulfuric acid, and acetic acid on the primitive tins and on the synthetic alloys he had prepared. His results indicated that HCl completely dissolved the primitive tins, without leaving any residue, it dissolved the tin in the alloys leaving a black precipitate of arsenic, weighing exactly as the original content; nitric acid reacted vividly with effervescence and transformed the metal into a white powder, and hot concentrated sulfuric acid dissolved the metal with release of  $SO_2$ ; after cooling, the limpid solution became semi transparent and gelatinous. Addition of water precipitated the metal as a white chalk. Acetic acid slowly corroded the metal producing a white chalk.<sup>20,22</sup>

Bayen drew the following conclusions: (a) heating all the Indies primitive tins in a closed vessel generated a white sublimate that was not arsenic, as claimed by Margraff; (b) treating the primitive tins with  $HNO_3$  demonstrated that they did not contain any of the metals or semi metals that the law allowed for the purpose of alloying, as well as none of the metals that potters added for the purpose of working the metal; (c) the primitive tins were dissolved completely by with HCl, without leaving a black powder; treatment of the alloys allowed discovering the presence of arsenic down to a content of 1/1024 parts; (d) the tins sold by honest traders did not contain arsenic.<sup>20,22</sup>

The second part of the report was a repetition of the above experiments using the tin imported from England and known in the trade as smoked salmon or baguette. It behaved the same as the previous primitive tins and their alloys, except that this tin was less pure, it contained arsenic in the ratios between 1/276 and 1/552 (an inoffensive amount), and a small little amount of copper and residues of the mining process. Bayen remarked that he did not pursue further the examination of the English tin because it was not imported into France.<sup>20,22</sup>

The third part of the report was devoted to the analysis of the tin worked and sold by the master potters. Here, Bayen repeated that since tin was a soft and very fusible metal, it was necessary to alloy with another metal, such as copper, zinc, bismuth, and antimony, in order to give solidity without making it fragile. Hence the first thing he did was to provide an analytical method for recognizing the presence of these metals, as well as a procedure for separating them (including silver), using aqua regia and HCl. In addition, he reported that the French tin originating from Cornouailles, contained arsenic in the proportion 1:763, and other metals, without health consequences.<sup>20,22</sup>

The fourth and last part of the monograph was a lengthy write-up in which Bayen answered the questions posed by the authorities. (a) Pure tin was not dangerous. Here Bayen gave a long historical review indicating that this was

assumed to be so by ancient works of the Greeks and Romans; (b) The least pure variety contained about 1/700 of arsenic, that is one grain of arsenic per ounce of tin per; an amount that was less poisonous than arsenic calx ( $As_2O_3$ ); (c) the experiments proved that the health of animals fed up 33 days with tin containing between 1/64 to 1/16 of arsenic (several times larger than the maximum arsenic content found in tin), was not affected; (d) utensils made from tin alloyed with the accepted metals and semi metals in the legal amounts (particularly copper, zinc, and bismuth) to give it the necessary ductility, were also non injurious to health. In addition, potters were prevented from using these metals in higher proportions because of their cost and because they made tin very fragile; (e) utensils made of tin lost very little weight even after a long use; the amount of arsenic mixed with the tin was so small that it had no action on the stomach; (d) the case of lead was different because of its low cost. Used in high proportions was not only a fraud, it was also dangerous to health.<sup>20,22</sup>

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