

JEAN-JACQUES COLIN

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RESUMEN. Jean-Jacques Colin (1784-1865), químico francés que realizó estudios fundamentales acerca de la fisiología de plantas, en particular germinación y respiración; el fenómeno de la fermentación, y la química del yodo durante la cual descubrió junto con Gaultier de Claubry, que el yodo era un excelente reactivo para determinar la presencia de almidón aun en pequeñas cantidades. Estudió también el efecto de diversas variables en la fabricación del índigo y jabones de diversas naturalezas.

ABSTRACT. Jean-Jacques Colin (1784-1865), a French chemist, who carried fundamental research on plant physiology, particularly germination and fermentation; the phenomenon of fermentation and the chemistry of iodine, during which he discovered, together with Gaultier de Claubry, the ability of iodine to detect starch even in very small amounts. He also studied the effect of variables on the preparation of indigo and soaps of several varieties.

LIFE AND CAREER

There is very little information about the life and career of Jean-Jacques Colin. He was born on December 16, 1784, in Riom, Department of Puy de Dôme, France, and passed away in 1865. Between 1810 and 1818 he served as répétiteur (1809-1817) of the course in chemistry given by Joseph-Louis Gay-Lussac (1778-1850) at the École Polytechnique. After the Restoration, when the new regime acted against those who were in favor of the Revolution, his salary at the École Polytechnique was reduced in half, from 1500 francs to 750 francs. In 1818 he resigned his position of répétiteur to take a position of professor of chemistry at the University of Sciences in Dijon. Colin also served as professor of chemistry at the École Royale Militaire de Saint-Cyr and was a corresponding member of the Société Philomatique.¹

SCIENTIFIC CONTRIBUTION

Colin wrote about 30 papers and books^{2,3} on the subjects of inorganic and organic chemistry, mineralogy, entomology, and plant physiology. In addition to the subjects described below, Colin also worked on cuprous salts and synthesized a new copper carbonate,⁴ on the burning of gunpowder,⁵ the nature and purification of pyroligneous acid (wood vinegar) and creosote,^{6,7} studied the means of protecting wheat from insects,⁸ found a new variety of euclase,⁹ studied the bleaching of candles,¹⁰ the presence of calcium carbonate in wines,¹¹ the habits of *Necrophorus cadaverinus* and *Spalotis praecox*,¹² etc.

The work of Colin with Pierre Jean Robiquet (1780-1840) about madder and the discovery of alizarin^{13,14} have been presented in another publication¹⁵ and will not be repeated here.

Plant physiology

Colin published several papers about physiological phenomena in plants and the preservation of wheat.¹⁶⁻²¹

Germination of seeds

Edwards and Colin believed that germination was affected by at least by three factors: heat, water, and air. No germination took place if one of them was missing.¹⁶ They wrote that the seeds of a large number of species floated in water because of the small air bubbles that attached to them. In this situation, the grains were subjected only to the three factors mentioned above; one part of the grain was exposed to the air and the other to the water. Floating enough grains of a given species allowed erasing the possible differences between the seeds (for example, volume). Edwards

and Colin believed that in this form it was possible to obtain comparable results on the effect of the different external factors.

In their first paper they reported the results of their experiments on the influence of temperature (heat) on germination.¹⁶ They mentioned that germination of wheat seeds in aqueous sugar was accompanied by a notable production of alcohol. This meant that the water had to contain ferment (yeast) among the substances excreted by the process. Since a large amount of sugar was known to be harmful to germination, this result seemed to indicate that the ferment was an accidental product originating from the action of the sugar. This supposition was found to be mistaken because germination experiments conducted during the hot season with corn grains suspended in distilled water had shown the presence of alcohol in an advanced state of the germination process, when the stem was green and well developed. This phenomenon increased as the ambient temperature became higher. In other words, the fermentation process excreted both the sugar and the yeast. Colin's previous finding that gluten was able to provide ferment substantiated this conclusion.²²

Edwards and Colin conducted a series of experiments with a variety of seeds to determine the lowest and the highest temperature at which the seeds were able to germinate. They found that most of the seeds of wheat, barley, rye, and beans, maintained for 15 min at the freezing temperature of mercury (-38.3 °C) [1] and then withdrawn, germinated the same as seeds maintained at room temperature. Additional results indicated that the seeds of winter wheat, barley, rye, and oats, were able to germinate in a soil maintained at 45 °C; most of the seeds did not ferment in a soil heated continuously at temperature levels between 45° to 48 °C, a temperature hardly occurring in soil.¹⁶

In a following publication Edwards and Colin wrote that the size (volume) of the seeds of winter wheat (*Triticum hybernum* L. subsp. *hybernum*) was larger than that of the seeds of March wheat (*Triticum turgidum* L. subsp. *turgidum*) and for this reason they had decided to study how this difference reflected in the germination and growth process of both varieties.¹⁸ For this purpose they selected 530 seeds of the first variety, having very large (relative) volume, and 530 of the second variety, without distinction of volume, and planted them at the end of April so that the effect of heat be more marked. Both varieties went through the initial stages of vegetation in the same manner, but surprisingly, the growth of the winter variety stopped at the grass stage and remained there, the plantlets presenting all the time several short stems and a large number of small leaves. The growth of the March variety followed the normal growth process all the way to maturity. Edwards and Colin carried a similar set of experiments using this time seeds of winter wheat having very small volume. This time they found that 60 out of the 530 seeds went through all the normal stages of growth. All these results seemed to indicate that the volume of the seed was a strong factor that affected the growth of plants subject to a high temperature environment. Edwards and Colin also planted seeds of the March variety in April, when the (initial) average ambient temperature was higher. Once again the phenomenon repeated itself: the plantlets remained in the grass stage and did not develop to full maturity. Additional experiences done with barley and rye showed the same behavior. Edwards and Colin concluded that the upper temperature limit for normal growth was not unique; it was different for each cereal. This allowed growing them for two different purposes, one year as animal food (grass stage) and the other, as human food (full development).¹⁸

Some years later Edwards and Colin published a more comprehensive version of this paper, including details about the observations reported by Jean-Baptiste Boussingault (1802-1887) and Alexander von Humboldt (1769-1859) about the growth of cereals at different altitudes of South America.²¹

Edwards and Colin also studied the influence of humidity on the germination of cereal seeds and found that this factor increased substantially the speed of the process. English colleagues informed them that the growth of many flower plants was also accelerated at higher humidity.²¹

Respiration

Edwards and Colin believed that the phenomenon of plant respiration was the most interesting subject of vegetable physiology.^{18,20} In spite of the many publications about its theoretical aspects it was hard to accept that the respiration of the seeds was the same as that of the leaves, and with the release of CO₂ associated with them. The respiration of the seed was assumed to be a simple phenomenon involving the combination of the oxygen of the air with the carbon of the seed, that is, only the atmosphere affected the seed, water played no critical role in respiration or, at the most, it helped the process. In the case of the leaves, carbon dioxide was released during the night and reabsorbed during the day, while oxygen was released under the direct rays of the sun. In a few words, the absorbed CO₂ was decomposed by the plant, which appropriated the carbon and disengaged the oxygen. To Edwards and Colin this explanation awarded the plant a power very hard to accept, including the fact that water took no part in the process. All these considerations led Edward and Colin to make their own study of the process.^{18,20}

Analysis of the information available showed that all the experiments had been carried in the air. Experiments conducted in water had been limited to the explanation of what took place in the air. The gas disengaged had not been analyzed and not quantified. For these reasons Edwards and Colin selected the following experimental apparatus and procedure: The tests were conducted in a bottle having a narrow neck and capable of holding 3 to 4 L of water. To the flask filled with water, they added 40 garden beans of a large size, without any fissure in the husk, or any other defect. The beans had previously been put in water and the whole shaken to eliminate all attached air. A bent tube filled with water was now connected to the neck of the flask and then introduced into a receiver full of the same liquid. In this closed arrangement the beans were in contact only with water and the retained air, which could not be removed. The

first phenomenon observed was the disengagement of air bubbles, originating from the beans. These bubbles were at first very small, little by little increasing in size until after 24 hours they were clearly visible. This phenomenon had never been reported before and was so extensive that it could not be attributed to the air contained in the beans. A repeated experiment done with beans cut through showed that the gas was clearly coming from the fundamental tissue of the seeds. Many of the beans were actually made to float by the air bubbles that adhered to them, and fell to the bottom as soon as the bubbles burst.^{18,20}

These experiments were conducted for at least four days. Afterwards, the beans were weighted to determine the amount of water they had absorbed, which turned out to be larger than their original weight. In order to determine if the beans were viable, they were planted together with a similar lot that had not been subjected to any experiment. All the beans germinated completely and developed radicles 9 to 10 mm long. The average net volume of gas developed by the process was found to be around 500 cm³, proving clearly that water played an active role in the germination process. This gas was shown to contain about 480 cm³ of CO₂, 25 cm³ of oxygen and about 35 cm³ which appeared to be nitrogen. To Edwards and Colin the large amount of CO₂ produced indicated that it had to come from one of the elements of water itself. This was a completely new fact: water had been decomposed and one of its elements, namely oxygen, had combined with the carbon of the seed to form CO₂.^{18,20}

At this stage of their experiments, Edwards and Colin were unable to determine exactly what had happened to the hydrogen liberated, and assumed that it had been partly or totally absorbed by the seed.^{18,20}

Fermentation

Colin wrote three memoirs and a letter on the subject of fermentation.²²⁻²⁵ The first one began with a short historical review of the fermentation of sugar, where he mentioned, for example, that Adamo Fabroni (1748-1816) had been the first to slice grape grains and notice that the sugar and the ferment were lodged in different cells and that fermentation did not take place unless the two lodges were broken.²⁶ This finding explained why there was little fermentation when the grains were left to themselves without being crashed. They would dry or decompose and the sugar and the ferment would deteriorate (putrefy) separately, without resulting in a regular fermentation. Fabroni also reported that tartar played an important role in the process of fermentation. Louis Jacques Thenard (1777-1857) established that all fruits having a juice capable of alcoholic fermentation, contained ferment, of which, beer yeast was the typical. This ferment had the property of transforming oxygen into CO₂, at room temperature and in a few hours.²⁷ Joseph-Louis Gay-Lussac (1778-1850) had reported that the process required the presence of air or oxygen and that action of the air could be replaced by a galvanic current.²⁸ Afterwards, Giochino Taddei (1792-1860) discovered that alcohol decomposed gluten into *gliadine*, soluble in alcohol, and *zymome* (vegetable fibrin), insoluble in alcohol.^{23,29}

Colin also mentioned that the Tatars used to produce spirits from cow or mare milk by souring it with an acid, and that he had found that honey could be made to ferment by the simple addition of water. He had conducted several experiments on the subject in the summer and found that: (1) fine wheat flour made into a paste without yeast became sweet within 36 hours and sour after some days. If used as yeast for a fresh paste; the latter quickly became sour and able to convert into alcohol a solution of 100 g of sugar in 400 g of water within one month; (2) 100 parts of sugar in 400 of water, mixed with 60 parts of fresh and well-washed gluten, became converted into alcohol in one month; (3) fresh beef converted the same sugar solution into alcohol within three weeks. The meat, separated by decantation and washed with water, was able to convert into alcohol a second equal quantity of sugar; although more slowly; (4) the white of an egg mixed with 500 parts of water and 100 sugar converted into alcohol after two months; (5) soft cow's cheese with herbs, well drained, left to itself for three days and dispersed in a solution of 100 g of sugar in 400 of water, fermented in three weeks. With buttermilk instead of cheese the fermentation was only partial because of the diluted state of the casein matter in it; (6) a solution of 100 g of sugar in a liter of night urine from a healthy person, fermented completely in one month; and (7) in the summer, a dilute solution of 30 g of isinglass (fish glue) mixed with 100 g of sugar, was able to ferment completely in four months.²³

Colin observed that the process was accompanied by disengagement of CO₂ and that alcohol was always obtained by distillation of the final mixture. Surprisingly, all the distillation residues were able to ferment again proving that alcohol and boiling stopped the process but did not destroy the cause. The same results were obtained when using yeast, albumen, new cheese, urine, albumen coagulated and putrescent, gliadine, tartarized gluten (i.e., gluten mixed with cream of tartar), tartarized albumen, pure fibrin, serum, blood coagulum and its coloring matter, etc.²³

Colin wrote that his results raised the possibility that many animal substances seemed to be able to induce alcoholic fermentation in sugar and that the process was slowed down with dilution. They also suggested the possibility that all nitrogenous substances could act as ferments. Colin speculated that "a ferment may be regarded as a substance, the presence of which determines a rupture of equilibrium; and, as the quantity of yeast generally employed is very small, such rupture cannot be understood, if it is not the result of a force the effects of which are transmitted by making the molecules of the fermentable substance pass in succession into a particular state; as, for instance, an electric force".²³ These ideas were written before Jöns Jacob Berzelius (1779-1848) described and defined catalysis and catalytic processes: "This is a new power to produce chemical activity belonging to both inorganic and organic nature...and the nature of which is still concealed from us. I...do not...imply that it is a capacity independent of the electrochemical properties of the substance...I am unable to suppose that this is anything other than a special kind of special manifestation of these, but as long as we are unable to discover their mutual relationship...it will also make it

easier for us to refer to it if it possesses a name of its own. I shall therefore...call it the *catalytic power* of the substances and decomposition by means of this *power catalysis*...Catalytic power actually means that substances are able to awaken affinities... by their mere presence and not by their own affinity. By means of these, the elements in a compound body rearrange themselves in another manner so as to achieve a greater degree of electro-chemical neutrality...On this occasion it is sufficient that the existence of catalytic power has been demonstrated with a sufficient number of examples...Turning with this idea to the chemical processes in living nature...we find that the insoluble starch in the tuber is changed to gum and sugar by catalytic power...living tissues".³⁰

According to Colin, beer yeast and grape sugar yeast were the most outstanding yeasts and for this reason he decided to study them in detail.²⁴ Beer yeast transformed the oxygen of the air into CO₂ and at the same time released by itself, a large amount of this gas, as Colin showed by the following experiment: A certain amount of the yeast was put in a capsule floating over mercury and enclosed inside a glass bell full of air free of CO₂ and connected to a system for measuring the gas released. The gas was forced to leave the bell by simply immersing the bell more deeply into the mercury. After seven and fifteen days the amount of CO₂ contained in the air was found to be 28.82 % and 34.94 %, respectively. In the last case, 13.94% of the CO₂ had to come from the ferment itself because the oxygen of the air could not have provided more than 21 %. The remaining yeast was partly liquefied, was acid but not putrefied, and was still able of converting the sugar into alcohol with facility.²⁴

Colin curved up in a ball the beer yeast and left it in the air by itself for three weeks and noted that its activity had reduced sensibly. He was not sure if this decrease was due to the long contact with air or to an internal alteration, in spite of the fact that the inside of the ball was probably without air or water. He believed that the actual phenomenon was due to an internal work, which continued until the yeast came in contact with sugar or had exhausted itself. This meant that contact with air (as claimed by Gay-Lussac) was not the reason of the activity; being in an ambient of adequate humidity and temperature probably caused it. Colin mentioned that the presence of water was necessary for sustaining the properties of the yeast; simple pressure of the yeast (to eliminate part of the water) resulted in a decrease of activity, and drying left it inactive. Nevertheless, boiling water retarded this activity. Colin added that the red oxide of mercury (HgO) paralyzed or destroyed the activity of the yeast.²⁴

In the following sections Colin studied the behavior of the water used to wash the yeast, the insoluble residue of the same, the extract of yeast, and the yeast of grapes. The water wash was able of fermenting sugar; when evaporated to dryness under cold and vacuum it left a yellow brown acid residue, having odor and flavor, lightly deliquescent, little soluble in alcohol and ether and did not contain CO₂ free or combined. The solid residue was acid; when humid it developed a cheese smell and had weak fermenting power. It behaved very similar to coagulated albumin. The yeast extract was a brown liquid smelling aromatic. Addition of diluted alcohol produced a grainy white precipitate unable to ferment sugar but becoming active after being in contact with water for sometime. This activity remained even after the solid had began to putrefy.²⁴

Colin extracted the juice of chasselas grapes (a variety of white grapes) and found that it converted sugar into alcohol, in closed bottles, that is, in the absence of air or oxygen, although with less power than beer yeast. An extract of this yeast fermented sugar initially very rapidly and then slowed down. An amount of 3.2 g was able to alcoholize completely 100 g of sugar.²⁴

Colin resumed his main findings as follows: (a) beer yeast and grape sugar yeast did not require oxygen to ferment sugar; (b) both yeast were composed of soluble and insoluble matter; (c) the fermenting power resided mainly in the soluble portion; (d) the insoluble portion had the ability of converting oxygen of the air into CO₂; (e) fermentation was produced by the joint activity of both portions; (f) this activity required an adequate temperature and the presence of enough water; (g) the activity suspended by the action of heat or boiling water could only be renewed with the help of oxygen or air; (h) the fermentation process of fruit juices, sweet saps, and mixtures of equal parts of sugar and the soluble portion of the beer and grape sugar yeast, followed the same path; (i) the same behavior was exhibited by all animal substances that could be classified as slow ferments; and (j) the fermentation process seemed to be initiated by electricity; this electricity was usually a result of the action of air upon the fermentable mixture.²⁴

In a letter to Gay-Lussac, Colin²² mentioned that during his research about fermentation he had noticed that during the digestion of albumen with sugar, water, and camphoric acid at a low temperature (but high enough to coagulate part of the albumen) the albumen acquired a blue color. He had also treated the albumen with diluted sulfuric acid and then concentrated the solution until it gelatinized. The material was then filtered and washed for a long time. After some days Colin noticed that the filter had become colored blue in some places and in others red and green. The same experiment conducted with HCl showed the appearance of a red color. This coloring process was similar to Vauquelin discovery that the waters of Vichy contained animal matter, which became blue in contact with acid. This suggested the possibility of reproducing the animal matter present in the waters of Vichy.²²

Colin, in his third paper published 17 years later, repeated with more detail his previous findings and this time mentioned Berzelius' explanation of fermentation as a catalytic phenomenon.²⁵ His mayor conclusions were as follows: (a) it was probable that albumin, gluten, cheese, urine, etc. activated the alcoholization of sugar by creating during their spontaneous putrefaction a substance that was the source of the phenomenon so that the existence of multiple ferments was only apparent; in reality the ferment was only one matter; (b) the presence of potassium bitartrate (cream tartar) accelerated the action of slow ferments, making the alcoholization faster and more complete; (c) the yeast was not albumin because its resulting products were of superior quality than those obtained from

coagulated albumin. In addition, dry yeast still contained soluble parts; (d) the yeast at 100 °C did not disengage hydrogen from water; (e) the extract of yeast was a soluble ferment; (f) the yeast of grape sugar contained potassium bitartrate; (g) fermentation generated yeasts, that is, substances that operated by themselves the transformation of sugar into alcohol, more energetically than the substances from which they originated; (h) the increase in cohesion produced by desiccation and the suspension of the spontaneous movement present in the original yeast, explained why dry yeast converted sugar to alcohol slower than the yeast in its original state; (i) on the one hand, substances devoid of nitrogen, such as starch, tannin, gums, etc. were unable of transforming sugar into alcohol; (j) on the other hand, the presence of nitrogen was not a sign of activity as a ferment; urea, quinine, uric acid, nasal mucus, etc. were unable of changing sugar into alcohol; (k) a large number of saline compounds retarded or stopped the fermentation process, for example, potassium nitrate, sodium chloride, dibasic calcium phosphate, and potassium bicarbonate; (l) fermentation was retarded by hydrogen sulfide, hydrogen iodide, and a few drops of nitric acid; (m) a microscopic examination of fresh winter yeast indicated that it was composed of round globules, three or four times smaller than the starch grains of wheat and barley; these globules were not broken by nitric acid and were tinted violet brown red; (n) a microscopic examination of an aqueous solution of the same winter yeast showed that the globules were not living animacules (microscopic animals). Consequently, fermentation could not be attributed to living entities; (o) living vegetables did not induce fermentation; and (p) Berzelius' catalytic theory did not contradict all the above facts.²⁵

Iodine

Bernard Courtois (1777-1838), a Parisian manufacturer of sodium carbonate (from calcined brown algae) and sodium nitrate, discovered iodine in 1811 during the treatment of the algae with sulfuric acid,³¹ an event that led to a flurry of papers reporting the properties of the new element and its chemical reactions, particularly the inorganic ones.³²⁻³⁶

Colin's paper reported the action of iodine upon ammonia, mercury, and different metallic oxides.³⁵ The first section of his memoir described the reaction between mercury and iodine. Courtois had found that mercury mixed with iodine in a proper ratio, changed to a very beautiful red powder; Colin verified this claim and found that when the mercury was in excess, the resulting product was either yellow or yellowish green, and that this result was independent of the presence or absence of air or water. The reaction of a mercury salt with an alkaline iodide produced a red precipitate if the mercury salt was present in very large excess and a yellow one if the iodide was present in a minimum amount. These precipitates were very comparable to the ones obtained with pure mercury. In addition, boiling in water some of the red precipitate and mercury changed its color to yellow; pouring on the yellow precipitate an alcoholic solution of iodine turned the color to a beautiful red. Upon heating, the red iodide of mercury changed to yellow, melted, vaporized and crystallized as rhomboidal leaves, which turned red when cooled. Colin remarked that the red precipitate contained double the amount of mercury present in the red one. He also described the reaction of these colored precipitates with a variety of reagents.

Courtois also reported that the reaction of ammonia and iodine produced a highly detonating substance; Gay-Lussac and Davy had obtained the same result and assumed that this substance was a product of the decomposition of ammonia.^{32,33} Colin carried additional experiments trying to determine the nature of this explosive. He first treated the substance with aqueous ammonia and observed that no gas was released and that the supernatant liquid contained some ammonium iodide, indicating that the substance contained an excess of ammonia. Heating this substance under water it decomposed partly, leaving a residue of iodine that afterwards sublimed. The remaining material was colored by ammonium iodide containing an excess of iodine. These results indicated that the fulminating powder was a combination of iodine, ammonia and nitrogen, or a simple mixture of the combinations of iodine with nitrogen and ammonia. Reaction of very dry ammonia gas with dry iodine produced immediately a very viscous and non-detonating liquid, which afterwards became less viscous, red brown, and smelling strongly to ammonia. This last combination was also not detonating, almost completely soluble in water and leaving a very fulminating residue. According to Colin, both liquids were only a combination of ammonia and iodine, in two different proportions.³⁵

Colin believed that water decomposed the ammonia combination into ammonium iodide and an iodine compound of nitrogen (nitrogen iodide) insoluble in alcohol and in water. Due to the affinity of ammonium iodide for iodine a portion of the iodine compound of nitrogen decomposed, a phenomenon that explained the observed continuous disengagement of nitrogen. This difference in solubility could be used to separate ammonium iodide from nitrogen iodide. Colin added that a low pressure was enough to cause the spontaneous explosion of the fulminating powder when dry, or when wet and even under water. Light was seen to accompany the detonation in the dark. He warned that these dangerous compounds should be handled with maximum care.³⁵

Colin also studied the solubility of iodine in a series of reagents: It dissolved easily in calcium and sodium bicarbonates, without disengagement of gas, but dissolved in ammonium bicarbonate it yielded a viscous non-detonating liquid. Iodine dissolved in alkaline iodides yielding iodized iodides, in the same manner that sulfur dissolved in sulfides yielding sulfurized iodides. Sulfur combined with iodine yielding a sulfide similar to that of antimony. Iodine also dissolved in aqueous nitric, sulfuric, and chlorhydric acids.³⁵

In a following paper Colin and Henri-François Gaultier de Claubry (1792-1878) wrote that all the reactions of iodine studied thus far have been done only with inorganic compounds,³¹⁻³³ and for this reason they had decided to

extend them to vegetable and animal substances.³⁶ For this purpose they used the three-tier classification of vegetable and animal substances proposed by Gay-Lussac and Thenard:³⁷ (1) substances composed of carbon, hydrogen, and oxygen, in the ratio they were present in water plus an excess of oxygen (that is, the acids); (2) substances composed of carbon, hydrogen, and oxygen, in the ratio they were present in water, that is, oils, vegetable acids, sugar, gums, starch, etc. (carbohydrates). This category included animal substances containing carbon, hydrogen, and oxygen in the ratio they were present in water (albumin, gelatin, fibrin, etc.), and nitrogen and hydrogen in the ratio present in ammonia; and (3) substances similar as those in the previous category but containing an excess of hydrogen (oils, camphor, etc.).³⁶

Colin and Gaultier de Claubry found that at room temperature vegetable substances of the first group did not react with iodine, they simple mixed; in the presence of boiling water iodine vapor was released and the resulting solution contained the corresponding vegetable acid. Heating a dry mixture of iodine and the vegetable substance resulted in the formation of abundant vapors of iodine and a solution containing a large amount of iodohydric acid (HI). Substances of the second group behaved differently: at room temperature they combined with iodine producing colored compounds; boiling water was able to release iodine vapors only when it was at 100 °C or the iodine was present in large excess. No hydrogen iodide was formed and the iodine seemed to combine with the vegetable substance without decomposition. Heating to the temperature of decomposition of the vegetable matter resulted in the formation of large amounts of vapors of hydrogen iodide. In the presence of water, substances of the third category reacted with iodine producing HI, which could be separated by water washes. Animal substances behaved in a similar manner; those that did not contain hydrogen in excess (e.g. gelatin and fibrin) did not release hydrogen iodide.³⁶

The second part of the memory was dedicated to a detailed account of the action of iodine on substances of the second group, the most notable of which was with starch.³⁶ Colin and Gaultier de Claubry remarked that triturating at room temperature a mixture of dry starch with dry iodine led the starch to assume immediately a violet color, which changed from blue to black, depending on its proportion in the mixture (red when using an excess of starch and black with an excess of iodine). This phenomenon was observed with starch of several origins, for example, from potatoes, salep, and the mucilage of the roots of marshmallow. The coloration disappeared only when the mixture was heated to the temperature of decomposition of the vegetable matter. At this temperature hydrogen iodide vapors formed mixed with the products of the decomposition of the organic matter (water, acetone, thick oils, and hydrocarbons). The compound of iodine and starch was only slightly affected by water at room temperature; the red compound was slightly soluble in water, the blue or black compounds dissolved easily upon agitation yielding, respectively, a blue or a colorless solution. In the latter case, the color reappeared on addition of nitric acid, concentrated sulfuric acid, or an aqueous solution of chlorine. The solution of the compound was decomposed by sulfur dioxide producing hydrogen iodide and sulfuric acid and precipitating the starch. Numerous compounds produced color changes, among them hydrogen sulfide, chlorine, potassium, sodium, and ammonium hydroxides, sodium or potassium bicarbonate, alcohol, etc. According to Colin and Gaultier de Claubry their results suggested the use of starch as a very sensitive reagent for discovering the presence of iodine, even in minute amounts.³⁶

Japanese indigo (*Polygonum tinctorium*)

In the initial stage of his research Colin published three short notes regarding the influence of air, its components, and several chemical reagents upon an infusion made with *Polygonum* leaves.³⁸⁻⁴¹ His main conclusions were as follows: (1) the rate of precipitation of the blue matter of indigo from air and its components decreased in the order nitrogen > air > oxygen; (2) pure oxygen and oxygen of the air were absorbed and then released as CO₂; nitrogen was not absorbed; (3) oxygen mixed with nitrogen induced a large precipitation of blue matter; (4) oxygen alone or open air did not produce the blue in the infusion of *Polygonum* made with boiling water, but both made the infusion blue with water at 65°C; (5) oxygen did not seem to be necessary for the formation of the indigo in *Polygonum tinctorium*; (6) sulfuric acid alone or with the addition of nitrogen produced only a purple red, which was probably the sulfo-purpuric acid of Dumas.⁴² Sulfuric acid on contact with the air or with oxygen, always produced blue in the aqueous infusions of *Polygonum*; (7) carbon dioxide could contribute to the formation of the blue matter but its extended action transformed the latter color into a beautiful carmine red color; (8) limewater deprived of air or in the presence of nitrogen, precipitated the infusions of *Polygonum* into a bluish or greyish white; in the presence of oxygen it generated green in the infusion made with boiling water and blue when water at 65°C was used; (8) indigo seemed to be present in the plant in such a state that it required the destruction or separation of the matter that accompanied it; (9) if the leaves used during the preparation of the infusion were left in the liquid, then, in addition to CO₂ and nitrogen, hydrogen was also disengaged in an amount of 25 to 50 % of the total gas liberated; (10) there was a substantial difference between the infusions prepared from the leaves of *Polygonum*, according to the temperature and the method employed for its preparation; (11) the easiest procedure for extracting indigo was using water at 65 °C (instead of boiling water); and (12) it was better to heat the mixture of leaves with water than to add the leaves directly into boiling water.³⁸⁻⁴¹

Colin and Labbé (a pharmacist) published a paper describing the principal methods used for extracting the indigo from *Polygonum tinctorium*.⁴³ A summary of these procedures was followed by a detailed description: (1) Procedure used in the French colonies: Here the leaves were macerated under agitation in water at room temperature until they began to ferment. At this moment the water was covered by a blue thick blue film. Addition of limewater caused the

immediate precipitation of the dye contained in the liquid; (2) the Alexander Edouard Baudrimont (1806-1880) procedure: In this method boiling water was poured on the leaves of *Polygonum*. After 24 hours the indigo was precipitated from the infusion by means of sulfuric acid; and (3) the Vilmorin procedure: the dry leaves were extracted with hot water and the dye precipitated by means of ferrous sulfate and calcium carbonate. This was probably the best procedure but it was very long and expensive.⁴³

Stain removal

In 1817 the Committee for the Dress and Equipment of the National Troops asked Colin to carry on experiments to determine plain and easy methods to remove spots of any kind off white uniforms. Colin was asked to address the following problems: (1) cleaning the whole dress of a soldier in white uniform; (2) removal of the stains of wine, red-fruits, colored liquids, and acid substances; and (3) removal stains caused by negligence and lack of cleanliness. Cadet de Gassinourt, head of the Committee des Arts Chimiques, published Colin's report after they repeated and confirmed Colin's results.⁴⁴

In order to carry on the pertinent experiments Colin stained the six pieces of white cloth that he received with ink, tallow, cerate, broth, oil mixed with wine, and oil mixed with emery. His first experiments showed that soap was able to remove all stains caused by fats; wine stains were not removed by chlorine but by sulfur dioxide; ink was partially removed by washing and by soap and by an aqueous solution of chlorine. Clothes treated with chlorine seemed to be perfectly white but upon drying they assumed a yellow tinge, which could not be removed by application of SO₂ vapors or by subsequent wash with soap. Colin then went on to describe a more specific treatment of each type of stain and the best method to remove or weaken it. For example, he tried unsuccessfully to remove wine stains with chlorine (in gas form or dissolved in water), sulfur dioxide, and an alcoholic solution of sulfur dioxide, alkalis, alkaline salts, and oxalic acid. Eventually he discovered that the spot could be completely removed by first washing the cloth with soap and water and then treating it with sulfur dioxide.⁴⁴

The committee awarded Colin 150 francs, in addition to covering all his expenses.

Soaps

Colin published one paper about the manufacture of hard soaps⁴⁵ and another about the manufacture of soft soaps.⁴⁶ In the first paper he first referred to the results obtained by Pelletier, D'Arcet, Le Lievre, Chevreul, and Braconnot, and then described the different raw materials (vegetable and animal) that were available for manufacturing soaps (i.e. olive, almond, rape, beech, and carnation oil, suet, fat, butter, fish oil, etc.). Afterwards he gave a thorough description of the twenty-four experiments he had carried to determine the guidelines for the manufacture of hard soaps. Colin reached the following conclusions: (1) the simultaneous action of air and aqueous vapor on oils removed their smell and color, prepared them to saponification, and above all, originated the remarkable phenomenon of separating the highly saponifiable part from the one that was less or non saponifiable. This separation occurred by treatment with sulfuric acid or by lowering the temperature; (2) the liquid part of oils could be obtained by a well-managed saponification; (3) water was absolutely necessary in the formation of soap because otherwise lime would not combine with the oil; (4) common salt not only could replace sodium carbonate but could also harden the soap as much as desired by partially or totally eliminating the water it contained. The whiteness and solidity of a soap depended on the manner in which it was separated from the colored waters in which it was formed; (5) increasing the amount of alkali employed made the bleaching process more difficult; (6) limewater played a critical role in saponification because it allowed the saponification of oils that refused to react with KOH or NaOH; (7) sodium salts decomposed easily soaps having other bases; this allowed converting hard soaps into soft soaps and the other way around; (8) removal of mucilage contained in the oil resulted in the production of oils of lesser quality; (9) the solid portion of oil gave soaps of better quality, with regards to whiteness, smell, and density; freezing seemed to lead the coloring matter to attach to the mother oil; (10) solid, and sufficiently hard soaps for the purpose of washing, could be obtained with every kind of oil; and (11) the best and the finest soaps, and the most difficultly altered, were those which have been made with oils not previously submitted to the action of any other ponderable body.⁴⁵

The second paper described the results of fourteen experiments conducted to determine the best conditions for manufacturing soft soaps.⁴⁶ According to Colin, the production of a good soft soap required controlling the amount of KOH used per unit weight of oil, soap with a high content of alkali was hygrometric and liquefied in a few hours, for example, using 180 g of KOH per 450 of linseed oil yielded soap that liquefied in two hours. Decreasing the amount of KOH to 139 g resulted in a yellow white soap, beautifully transparent and having an appropriate consistency that in contact with humid air did not change for a long time. Colin warned against using alkali imported from America because it produced a hazy soap. The ingredients used to produce the desired soap should not be added simultaneously to the boiler because it resulted in a very viscous mixture, which became highly foaming when reaching its boiling temperature.⁴⁶

BIBLIOGRAPHIC REFERENCES

1. Azzola O. Archivist, Bibliothèque Central, École Polytechnique, Paris, personal communication, 2016.
2. Colin J J. *Cours de Chimie à l'Usage de MM. les Élèves de l'École Militaire de Saint-Cyr*. Thomine, Paris, 1827.
3. Colin J J. *Considérations Élémentaires sur les Proportions Chimiques, les Équivalents et les Atomes, pour Servir d'Introduction à l'Étude de la Chimie*. Gauthier-Laguionie, Paris, 1841.
4. Colin J J. Taillefert M. Note Relative à Quelques Observations sur les Sels Cuivreux, où l'on Fait Connaître une Nouvelle Variété de Carbonate de Cuivre Artificiel qui a son Analogue dans la Nature. *Ann Chim.* 1819: 12; 62-68.
5. Colin J J. Taillefert M. Note sur le Poudre à Tirer. *Ann Chim.* 1819: 12; 387-398.
6. Colin J J. Mémoire sur la Nature et Purification de l'Acide Pyro-ligneux. *Ann. Chim.* 1819: 12; 205-215.
7. Colin J J. Travaux sur la Créosote. *Mém Soc Sci Natur Seine-et-Oise.* 1835: 1; 191-197.
8. Colin J J. Notice sur le Blé Avarié par les Insectes et les Moyens de l'en Préserver. *Mém Soc Sci Natur Seine-et-Oise.* 1835: 1; 165-190; published as booklet by Montalant-Bougleux, Versailles, 1835.
9. Érambert A. Colin J J. Note sur une Nouvelle Variété d'Euclase, *Mém Soc Sci Natur Seine-et-Oise.* 1835: 2; 203-206.
10. Colin J J. Du Blanchiment des Cires Rebelles. *Mém Soc Sci Natur Seine-et-Oise.* 1842: 2; 199-202.
11. Colin J J. De la Présence du Phosphate de Chaux dans les Vines. *J Pharm.* 1844: 5; 351-352.
12. Colin J J. Sur le Moeurs du Necrophorus Cadaverinus et Spælotis Præcox. *Ann Soc Entomol.* 1847: 5; 110-11.
13. Robiquet P J. Colin J J, Sur un Nouveau Principe Immédiat des Végétaux (l'Alizarin) Obtenu de la Garance. *J Pharm.* 1826: 12[2]; 407-412.
14. Robiquet P J. Colin J J, Nouvelles Recherches sur la Matière Colorante de la Garance. *Ann Chim Phys.* 1827: 34[2]; 225-253.
15. Wisniak J. Pierre-Jean Robiquet. *Educ Quím.* 2013: 24(núm. extraord. 1); 139-149.
16. Edwards W F. Colin J J, De l'Influence de la Température sur la Germination. *Ann Sci Natur Biol.* 1834: 1, 258-270.
17. Edwards W F. Colin J J, Mémoire sur la Végétation des Céréales Sous Hautes Températures. *Compt Rendus.* 1836: 2; 121-125.
18. Edwards W F. Colin J J, Sur les Effets de la Vapeur dans Toutes les Périodes de la Végétation. *Compt Rendus.* 1837: 4; 496-503.
19. Edwards W F. Colin J J, Sur la Respiration des Plantes. *Compt Rendus.* 1838: 7; 922-927; published as booklet by Montalant-Bougleux, Versailles, 1838.
20. Edwards W F. Colin J J, Sur la Respiration des Plantes. *Mém Soc Sci Natur Seine-et-Oise.* 1842 : 2; 53-60.
21. Edwards W F. Colin J J, Mémoire de Physiologie Agricole. Sur la Végétation des Céréales sous de Hautes Températures. *Mém Soc Sci Natur Seine-et-Oise.* 1842: 2; 207-232.
22. Colin J J, Lettre de M. Colin à M. Gay-Lussac. *Ann Chim.* 1825: 30; 321-324.
23. Colin J J, Mémoire sur la Fermentation du Sucre. *Ann Chim.* 1825: 28; 128-142.
24. Colin J J, Mémoire sur la Fermentation. Deuxième Part. *Ann Chim.* 1825: 30; 42-64.
25. Colin J J, Nouveaux Mémoire sur la Fermentation. *Mém Soc Sci Natur Seine-et-Oise.* 1842: 2; 1-43.
26. Fabroni A. Dell'Arte di Fari il Vino per la Lombardia Austriaca. Grazioli, Firenze, 1787.
27. Thenard L J. Sur la Fermentation Vineuse. *Ann Chim.* 1803: 46; 224-230.
28. Gay-Lussac J L. Sur la Fermentation. *Ann Chim.* 1810: 76; 245-260.
29. Taddei G. Delle Modificazioni che Insorgono nella Farina di Frumento Impastata con Altre Sostanze Vegetabili. Brugatelli G. 1819: 2; 283-292.
30. Berzelius J J. Sur un Force Jusqu'ici Peu Remarque qui est Probablement Active Dans la Formation des Composes Organiques, Section on Vegetable Chemistry. *Jahresber.* 1835: 14; 237.
31. Clément N. Découverte d'une Substance Nouvelle dans l'Vareck par M. B. Courtois. *Ann Chim.* 1813: 88; 304-310.
32. Gay-Lussac J L. Mémoire Sur l'Iode. *Ann Chim.* 1814: 91; 5-160.
33. Davy H. Some Experiments and Observations on a New Substance which Becomes a Violet-Coloured Gas by Heat. *Phil Trans.* 1814: 104; 74-93. Read January 20, 1814, from a letter dated, December 10, 1813, Paris.
34. Vauquelin L N. Expériences sur l'Iode. *Ann. Chim.* 1814: 90; 206-223, 239-251.
35. Colin J J. Sur Quelques Combinaisons de l'Iode. *Ann Chim.* 1814: 91; 252-272.
36. Colin J J. Gaultier de Claubry H F. Mémoire sur les Combinaisons de l'Iode avec les Substances Végétales et Animales. *Ann. Chim.* 90, 87-100, 1814, published as a booklet by Perroneau, Paris, 1814.
37. Gay-Lussac J L. Thenard L. J. Extrait d'un Mémoire sur l'Analyse Végétale et Animale. *Ann Chim.* 1810: 74; 47-64.

38. Colin J J. Expériences Concernant l'Influence de l'Air et de ses Éléments, l'Oxygène et l'Azote sur l'Infusion du Polygonum Tinctorium. *Compt Rendus*. 1839: 7; 565.
39. Colin J J. Nouvelles Recherches sur le Polygonum Tinctorium. *Compt Rendus*. 1839: 9; 774.
40. Colin J J. Nouveaux Essais sur le Polygonum Tinctorium. *J Chim Méd*. 1840: 6[2]; 1170.
41. Colin J J. Nouveaux Essai sur le Polygonum Tinctorium. *Mém Soc Sci Natur Seine-et-Oise*. 1842: 2; 105-115.
42. Dumas J B. Sur la Nature de l'Indigo et sur la Véritable Composition de Quelques Produits Auxquels il Donne Naissance. *Comptes Rendus*. 1836: 3; 743-747; *Ann Chim*. 1836: 63; 265-272.
43. Colin J J. Labbé A. Notice sur l'Extraction de l'Indigo du "Polygonum Tinctorium". *Mém Soc Sci Natur Seine-et-Oise*. 1842: 2; 81-103.
44. Colin J J. Sur les Moyens d'Enlever les Taches sur les Habits de Drap Blanc. *Bull Soc Encour Ind*. 1818: 153; 48-54.
45. Colin J J. Expériences Relatives à la Fabrication des Savons Durs. *Ann Chim*. 1816: 3; 5-25.
46. Colin J J. Expériences Relatives à la Fabrication des Savons Mols. *Ann Chim*. 1821: 16; 297-304.