THE CONTRIBUTIONS OF PAYEN AND LABILLARDIÈRE TO THE DEVELOPMENT OF COLORIMETRY

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Two very important contributions to the development of colorimetry are identified with the 17th century. In 1729, the French mathematician and astronomer Pierre Bouguer (1698-1758) published the work *Essai sur la gradation de la lumière*. In the section where he studied transparency and opacity, he finished by concluding that when light crosses a transparent medium, it diminishes in geometric progression to the thickness of the medium crossed (1). Thirty years later, in 1760, the German Johann Heinrich Lambert (1728-1777) rediscovered Bouguer's ideas independently and published the work *Photometria sive de mensura et gradibus luminis, colorum, et umbrae* (2). It is advisable however to note the different positions held by each work: while Bouguer carried out a physical analysis, centered exclusively on the characteristics of an optical system, Lambert developed relative structural concepts about the nature of the matter, accepting a distribution of particles in a medium, and attributing the light absorption to the mentioned particles. Lambert's interpretation also had a greater mathematical emphasis, in which he proposed two basic theorems (sections 876 and 877 of his *Photometria)* (3).

The experiments of Bouguer and Lambert on the absorption of light were restricted to transparent solids. It was not until 1852 that the conclusions of Lambert about the absorption of light were extended to colored solutions. Two authors, Félix Bernard (4) and August Beer (5), independently and within a few months of each other, published doctoral dissertations in which they stated that concentration in colored solutions plays the same role as opacity in transparent solid media. In both works the notion was introduced of the coefficient of absorption, being characteristic of the material studied.

These initial contributions serve as a foundation for the later contributions to the development of colorimetric methods Payen and Labillardière. Although some authors (6) place the origin of colorimetry in the 1830s, recently there has been an investigation into the existence of procedures and apparatus used prior to this (7-11).

The beginnings of volumetric analysis: Determination of chlorine dissolved in water

The use of chlorine to bleach cloth, according to the procedure of Berthollet, coincided with its discovery by Scheele in 1774. Technicians, interested in this process for its possible application to industry, began designing variations of the method very quickly. Before 1789 a French chemist, Henri Descroizilles, had also encountered the new bleaching procedure. Concluding that its effectiveness depended on the chlorine concentration in water, he designed a procedure to measure the chlorine content by making use of the property of hypochlorite to decolorize solutions of indigo in sulfuric acid (12). The resolution of this problem required the design of a glass instrument (Fig. 1), on which he marked a scale with hydrofluoric acid to quantify the results. In Fig. 1, three pieces are distinguished (sectors 1-3): the first represents the "buret," in the author's nomenclature, although it would currently be the "test tube" or "graduate cylinder." The second, given the name "mesure," is a pipet. This utensil is inserted into chlorine water until the liquid reaches mark A. The upper opening is then sealed with the finger, and later the volume of liquid is poured into the graduate cylinder until it reaches the zero level. The third piece represented is a suction pipet containing a fixed quantity of indigo, which is then poured little by little into the graduate cylinder. The different pieces are inserted in a receiving vessel that contains the solutions to be analyzed. A diagram of the instruments is shown in Fig.1 (sectors 4-7). This is probably the first well-known case of an apparatus designed for quantitative analysis. The first description of Descrozilles's method, however, was given by Berthollet in 1789 in an article in which he described his own procedure for bleaching cloth (13). According to Szabadvary (14, p 210) Berthollet and Lavoisier had already used the reaction between chlorine and indigo in 1788 to estimate the color intensity in indigo samples. Berthollet's description of Descroizilles' procedure, carried out in 1789, did not correspond to the author's description of the one carried out later in 1795. In this case, the indigo is poured into the chlorine water.

Other European authors independently described the same method, introducing variations on the initial model published in 1789. Berthollet himself (13, p 177) pointed out that Descroizilles' procedure, which he named "Berthollimétre," was used by Watt, who employed cochineal in place of indigo. Among all the technical innovations based on Descroizilles' work, it is important to highlight the proposals between 1815 and 1826 of other French chemists who improved substantially the original procedure, to which was given the name "chlorometres." Thus, Welter (1817) (15), Gay-Lussac (1824) (16), and Henry and Plisson (1826) (17) all published works about "chlorometres." They all focused their objective on the quantification of the indigo decolorization process with sulfuric acid. However in 1824 another French chemist, Houtou de Labillardière, substituted starch-iodide for indigo in order to design an alternative procedure to estimate the chlorine content in commercial calcium hypochlorite. This procedure was based on the ability of the starch-iodide complex to turn blue in an acid medium (18). Hotou of Labillardière was the first to use the iodine-iodide system in volumetric analysis, thirteen years after the discovery of iodine by Bernard Courtois.

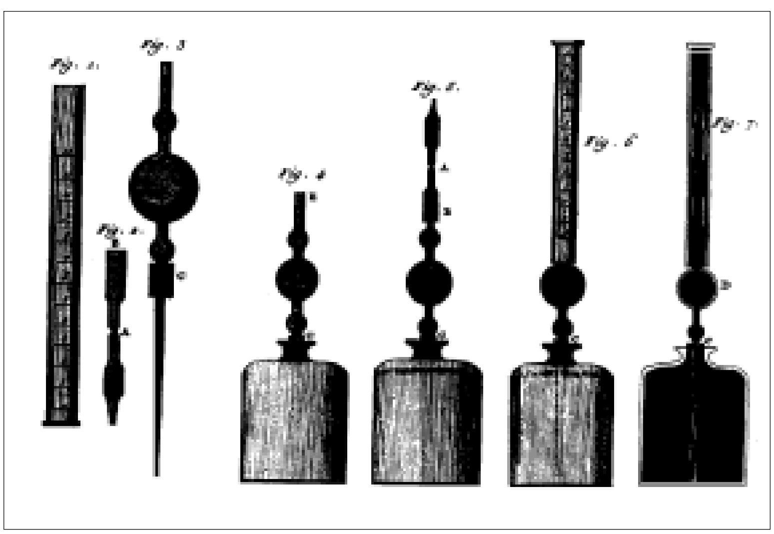

Figure 1. Descroizilles' glass instruments

The means by which Labillardière's method was made public was very bizarre, and it caused a great deal of controversy between Labillardière and Payen. News of this procedure was reported in the March 1826 issue of the *Journal de Chimie Médicale, de Pharmacie et de Toxicologie* by Julia de Fontenelle (19), and also in the session of the Paris Société Philomatique, where Payen was present. Pierre Jean Robiquet, the Société Philomatique secretary, presented Labillardière's method, as is verified in the *Journal de Chimie Médicale, de Pharmacie et de Toxicologie* May issue (20). A concise description of this procedure appeared in the Fontanelle abstract. Later, in a meeting of the Société Philomatique, Anselm Payen criticized the method, while Robiquet defended Labillardière. This prompted Labillardière to publish a note in the May 1826 issue of the *Journal de Pharmacie et des Sciences Accesoires* (18), in which he criticized Descroizilles' method as being imprecise. He pointed out that he had built his apparatus two years previously, on April 2, 1824, at the Rouen Academy. The question of these dates is very important because in the same text he complained about the treatment accorded his own work, as well as the suggestion that Gay-Lussac had already designed a similar procedure. After detailing his procedure, he concluded with some derisive comments directed at Payen (18):

En effet, on a dû s'étonner comme moi que M. Payen, l'un des collaborateurs du Dictionnaire technologique et auteur d'un traité des réactifs, n'ait pas prévu l'utilité du sel marin dans la liqueur d'épreuve, et sourtout n'ait pas fait la remarque que je faisais les essais, non sur le chlore, mais bien sur le chlorure de chaux. En

> consultant le Traité de chimie élémentaire de M. Thenard, 4e édition, tome II, pag, 191, il pourra voir que le mélange de chlore et d'acide sulfureux dissous se transforme tout à coup en acide sulfurique et en acide hydrochlorique par la décomposition de l'eau.

Payen was not intimidated by this attack, immediately submitting a note to the Société de Pharmacie, which was published in the June issue of the *Journal de Pharmacie et des Sciences Accesoires* (21). The following text is an extract of this note:

> Le fait que j'ai annoncé de la décoloration par l'acide sulfureux de l'amidon bleui est vrai, mais cet acide ne peut exister en contact avec le chlore que dans le cas où l'un et l'autre sont anhydres, ce qui n'était pas dans l'application que j'en ai faite par inadvertance. Quant à l'utilité dont pourrait être la solution du sel marin, dans la liqueur d'épreuve, aucun des chimistes auxquels j'ai eu l'occasion d'en parler, et bien d'autres sans doute, ne s'en étaient pas douté avant l'explication donné par M. Hotou-Labillardière.

This confrontation between Payen and Labillardière had a postscript in the following year when Henry presented Labillardière's colorimeter in the *Journal de Pharmacie et des Sciences Accesoires* and in a footnote, affirmed (22):

> Le décolorimètre de M. Payen pour essayer la force des charbons était composé d'un appareil á peu près semblant.

Coal as a decolorizing substance: Bleaching of sugar

In 1785, the German-Russian chemist Johann Lowitz, while trying to obtain a crystalline form of tartaric acid, noticed that coal powder, which had inadvertently contaminated a solution of the acid, had very effectively eliminated the impurities in the solution. This accidental discovery led to a planned series of experiments on the decolorization of certain substances of vegetable or animal origin with vegetable and animal coal. As a result of all of these experiments, Lowitz concluded that coal decolorized some solutions and also eliminated suspended impurities and the inherent odor in the solutions. Consequently, he recommended the use of powdered coal as a purifying agent in the production of vodka and sugar syrup and in the treatment of water for human consumption. Lowitz's work generated interest from many pharmacists and chemists. In 1811, Cadet de Gassicourt (23) and Pierre Boullay (24) published reviews, in which they described various studies on the decolorizing and bleaching properties of vegetable and animal coal. Boullay credited Figuier (25, 26) with the discovery in animal coal of a greater bleaching power for colored liquids.

In the second decade of the nineteenth century, the use of animal coal in industrial decolorizing and bleaching processes was increasing; as a result the production of coal was gaining greater economic importance. In

DÉSIGNATION de l'espèce de charbon employé.	POIDS du charbon.	QUANTITÉ de liqueur d'essai d'indigo décolorée.	QUANTITÉ de liqueur d'essai de mélasse décolorée.	Expression numérique de la force décolorante du charbon sur l'indigo.	Expression numérique de la force décolorante du charbon sur la mélasse.
Sang calciné avec la potasse.	1 gramme.	1 litre 6	0, 18	50	20
Sang calciné avec la craie.	id.	0,57	0, 10	18	11
Sang calciné avec le phosphate de chaux.	id.	0,38	0, 09	12	10
Gélatine calcinée avec la potasse.	id.	1,15	0, 14	36	15, 5
Albumine calcinée avec la potasse.	id.	1,08	0, 14	34	15, 6
Fécule calcinée avec la potasse.	id.	0,34	0, 08	10, 6	8, 8
Charbon de l'acétate de potasse.	id.	0,18	0, 04	5, 6	4, 4
Charbon obtenu de la décomposition du sous-carbonate de soude par le phosphore.	id.	0,38	0, 08	12	8, 8
Noir de fumée calciné.	id.	0,128	0, 03	4	3, 3
Noir de fumée calciné avec de la potasse.	id.	0,55	0, 09	15, 2	10, 6
Charbon des os traité par l'acide muriatique et par la potasse.	id.	1,45	0, 18	45	20
Charbon des os traité par l'acide muriatique.	id.	0,06	0,015	1,87	1, 6
Huile végétale ou animale calcinée avec le phosphate de chaux.	id.	0,064	0,017	2	1, 9
Charbon des os brut.	id.	0,032	0,009	1	1

Figure 2. Bussy's Scale

keeping with this, Cadet de Gassicourt published an article in 1818 (27) detailing the different methods of obtaining coal, as well as some of its more important applications. Among these, he highlighted its use in the sugar beet industry, introduced by Monsieur Magnes and Charles Derosne (28). One question of economic importance remained unanswered: which type of coal had the greatest bleaching power?

Because of the uncertainty about the chemical behavior of coal in liquid solutions, the Société de Pharmacie of Paris decided in 1821 to offer a prize of six hundred francs for solutions to the following (30):

1. To determine the way in which coal operates in the decolorizing process.
2. To investigate the influence exerted by the other trace substances in the coal.
3. To investigate whether the physical state of the coal is important in the decolorizing process.

Seven entries were received for this competition, although one was submitted before the opening date. Antoine Bussy, Professor of the School of Pharmacy of Paris, was awarded first place, and second place went to Anselm Payen (31). Both reports, published in the 1822 May-June issue of the *Journal de Pharmacie et des Sciences Accésoires*, included a study of specific procedures for making comparisons in the bleaching powers of different coals.

In Bussy's work the system for evaluating the bleaching strength of coal was based upon its capacity to decolorize indigo in sulfuric acid. Indigo was chosen for its important properties: the quantity of indigo could be measured accurately; the bleaching point could be observed with certainty; and the indigo dye was unaffected by light or other factors. The author provided the following description (32):

> C'est ainsi que j'ai reconnu que la dissolution qui m'a servi pour mes essais contenait un millième de son poids d'indigo. Pour essayer un charbon avec cette dissolution, j'en prends une certaine quantité que je mets dans une fiole, en contact avec une quantité connue de charbon; je chauffe légèrement, ce qui hâte un peu la décoloration, et j'ajoute de la liqueur d'essai jusqu'à ce que le charbon refuse de la décolorer.

Bussy carried out experiments with molasses solutions in order to determine whether the relative order of decolorizing power remained the same when the coal passed from one colored solution to another. Using 1 gram of each coal sample, he compared their bleaching power against that of bone black (*Charbon des os brut*), to which he arbitrarily assigned the value of 1. These results, expressed in table form, are reproduced in Fig 2.

Payen's work (33) was less systematic than the Bussy's. He carried out a series of experiments from which he tried to answer the three basic questions of the competition. He failed, however, to describe procedures for establishing the comparative bleaching power of various coals. In a footnote he observed (33):

> Je me propose de publier un instrument (decolorimètre) à l'aide duquel j'obtiens la mesure exacte des actions décolorantes. Sa construction es fondée sur ce que l'intensité des couches colorés est en raison inverse de leur épaisser; ainsi, en prenant pour unité una nuance quelconque, on obtiendra tous les multiples, tous les rapports possibles de cette nuance à tous les autres; il suffit pour cela de mesurer exactement la hauteur perpendiculaire entre deux plans diaphanes qui comprennent le liquide coloré ramené à l'unité de nunce au moyen de l'espace augmenté ou diminué entre les deux plans.

Payen's approach was illustrated in his *Traité Élémentaire des Réactifs* (34), where he gave a description of his apparatus, represented in Fig. 3. The analysis procedure was based on a visual comparison. In the small cylinder P, the standard solution is introduced along with 10 grams of a sugar solution and 1000 grams of water. The test solution is combined with 1 deciliter of standard solution and 2 grams of coal; the mixture is filtered and the filtrate introduced into the vertical tube DC. As the mobile piston BB is slowly withdrawn, the test solution falls into the fixed horizontal tube AA, and

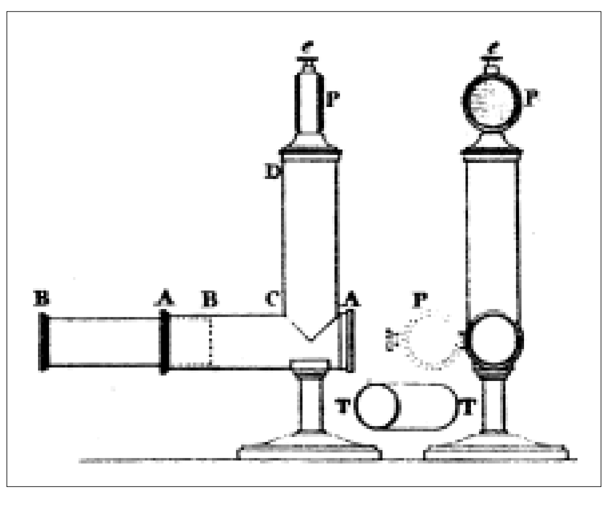

Figure 3. Payen's decolorimeter.

the optical path between the lenses in the right ends of the tubes BB and AA is increased. The piston BB is withdrawn until the color of the test solution is equivalent to that of the standard in small cylinder P. Since the mobile piston has a graded scale, it is possible to determine the distance between the lenses of tubes BB and AA. Each centimeter of the scale of tube BB is equal to the thickness of cylinder P. Thus, it is possible to make a relatively precise comparative table of the decolorizing power of different coals.

In 1827, Labillardière also used the absorption of light through a transparent colored solution to determine the bleaching power of commercial products. In spite of this, Snelders (6) says that Keates (1830) and Lampadius (1838) carried out the first colorimetric experiments, but it is evident that the credit for this should go to Labillardière, who designed his "colorimètre" for this purpose. Although the first report of his apparatus and procedure appeared in a paper published by the author in 1827 (35), an account written by Henry appeared in *Journal de Pharmacie* in the same year (22). (The authors have been unable to gain access to the former publication). A new description appeared one year later in a paper published in *Annales de l'Industrie française et étrangére*. This article was also reproduced in the work "Traité complet des propriétés, de la préparation l'emploi et des Matières Tinctoriales et des Couleurs" by Leuchs (36, 37). Labillardière justified the determination of the coloring capacity of various raw materials used in industrial dyes in order to evaluate their economic worth. He explained Descroizilles's procedure, later modified by Welter and Gay-Lussac, which was based on the time required to decolorize raw materials with chlorine. He refused to use this imprecise method because chlorine can act upon the coloring substances and also other substances present in raw materials.

Labillardière's central idea was to see whether he could transfer the successful results from the test tube to fabrics and other materials. In order to do so, he designed a black box through which he could compare two colored solutions, one of the dye and the other of the standard. He named this instrument "colorimètre." His arrangement must be similar to the one depicted in Fig. 4, reproduced according to the author's description. Later this was illustrated in some texts (38, 39, 40). We have found three different illustrations, two of which are shown in Figs. 5 and 6.

The method for using the apparatus is described in the instructions below (36):

> Après voir traité ou dissous comparativement dans l'eau, ou tout autre liquide convenable, des quantités égales de matières tinctoriales, on introduit de ces dissolutions dans les tubes colorimetriques jusqu'au zéro de l'échelle supérieure; on les place ensuite dans la boîte par les deux ouvertures pratiquées à cet effet, et, après avoir comparé leur nuance, si on trouve une différence, on ajoute de l'eau à la plus foncée, et l'on agite ensuite le tube après avoir bouché l'extrémité avec le doigt; si après cette addition d'eau on remarque encore une différence, on continue d'en ajouter jusqu'à ce que les tubes paraissent de la même nuance. On lit ensuite sur le tube dans lequel on a ajouté de l'eau le nombre de parties de liquide qu'il contient; ce nombre comparé au volume de la liqueur contenue dans l'autre tube (qui est égal à 100), indique le rapport entre le pouvoir colorant ou la qualité relative de deux matières tinctoriales; et si, par exemple, il faut ajouter à la liqueur la plus intense 25 parties d'eau pour l'amener à la même nuance que l'autre, le rapport au volume des liqueurs contenues dans les deux tubes sera comme 125:100; et la qualité relative des matières colorantes sera représentée par le même rapport, puisque la quotité de ces matières est proportionelle à leur pouvoir colorante.

The author recommended several precautions to assure dependable results: exhaustive drying of the test tubes,

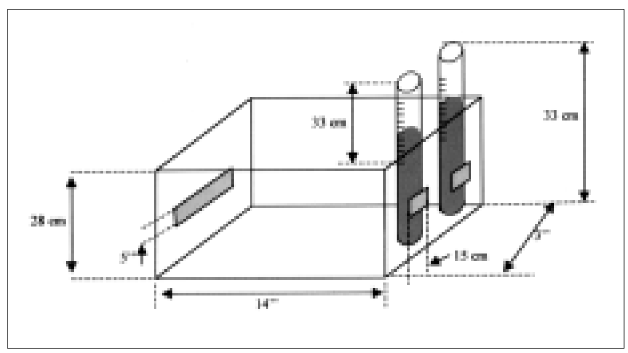

Figure 4. Labillardiere's colorimeter (from Labillardiere's description)

avoidance of contamination of the tubes by handling, blackening of the box, and the use of homogeneous light of appropriate wave length for various coloring substances. Finally, it is important to highlight Labillardière's thought (36) that the method could be generally applied to different coloring materials but specifically to cochineal. It is not surprising that Girardin (41) put this generalisation into practice, for it was he (38) who described the apparatus and provided a graphical illustration (Fig. 6). He himself applied the procedure to the analysis of indigo, cochineal, and bija, the

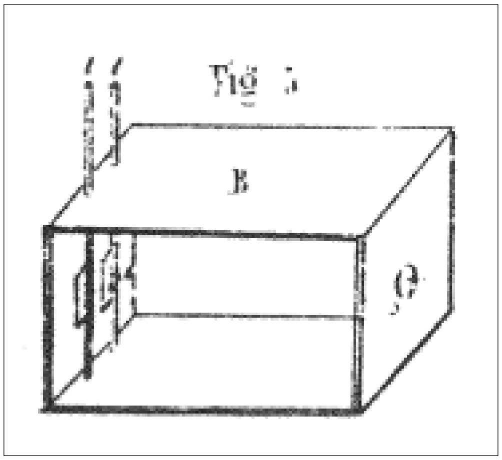

Figure 5 Labillardiere's colorimeter (from a paper by Chevallier)

common name given to the bixaceas species, better known as Achiote. In his text Girardin explicitly recognises Labillardière as the inventor of the apparatus.

A. Payen

Anselm Payen was born in Paris on January 17, 1795, son of the owner of an ammonium chloride factory. This product was made from animal waste from a slaughterhouse situated in Grenelle, a small village within the parish of Vaugirard. In this village, just as in the village of Javel on the outskirts of Paris, in which the Count d'Artois had established an acids and mineral salts factory, a chemical and food processing industry was emerging at the end of the 18th century. In 1824, as the importance of this industry was growing, a group of investors decided to establish an industrial town in this location; and so the village of Grenelle separated itself from the parish of Vaugirard in 1830 (50).

Payen's father forbade his son to attend school, insisting instead that he be educated at home. This meant that Payen was reared with a very strong scientific background and in an environment almost completely devoid of social contact with people of his own age. Possibly because of this he grew up to be a very ill natured man. He studied chemistry under the supervision of Vauquelin and Chevreul (49) and later, at the age of twenty, he went on to manage a sugar beet factory at Vaugirard (50). However, Payen considered this position as more a part of his family's industrial activity. In his prize-winning paper (33) of 1822, he chose to introduce himself as "fabricant de sel amoniac."

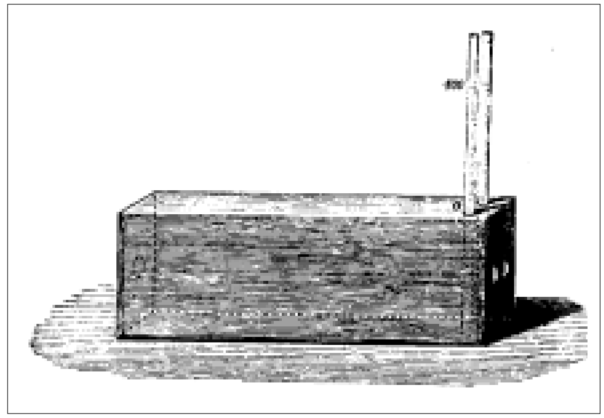

Figure 6. Labillardiere's colorimeter (from a paper by Girardin)

In the early 1820s he became interested in beer making in France. Payen and Chevalier published a paper describing the possibility of cultivating hops in Grenelle and in Vaugirard (29) for use in the making of beer. His first successful industrial venture was the manufacture of borax, which until then had been imported and about which he published various papers (51).

In 1829 Payen began to teach industrial chemistry at the École Centrale des Arts et Manufactures and ten years later he occupied a similar chair at the Conservatoire des Arts et Métiers. From 1842 Payen became a much more prominent figure in the academic world and was also made "Honour Legionkavalier," although he did not abandon his industrial interests. He wrote a large number of papers, most of which were concerned with the food industry. A complete bibliography of Payen's works is to be found in two reference sources (51, 52). His investigations revealed flaws in some industrial processes. For example, his studies on the analysis of wheat and other cereals forced a change in the method of bread making. His main contribution, in collaboration with Persoz, was work with carbohydrates between 1834 and 1835, involving hydrolysis of starch and its subsequent transformation into sugar by the action of a malt-containing substance they called diastase. These chemical processes were at the core of a controversy with Guerin-Varry, who claimed to have discovered them. Also interested in the study of plants, he discovered that the chemical composition of starch was independent of the plant from which it was obtained. He also characterised an isomeric starch obtained from woody plants, which he named cellulose, and achieved the separation from cellulose of another substance he named "lignina."

Until his death on May 13, 1871, Payen lived in a working-class suburb of Paris and was known for his dedication to teaching. In spite of ill health, he continued giving classes until one day when he collapsed in the classroom, two years before his death. He died during the "Comune" and was afforded a simple funeral.

François Joseph Houtou de Labillardière

François Joseph Houtou de Labillardière was born in Alençon (l'Orne Département, Normandy) on April 1, 1796 of a small, middle-class family. Although little is known about his parents, his grandfather, Michel Jacques Houtou, was the master of La Billardiere and his grandmother, Madeleine Jeanne Lepin, was a manufacturer and trader of handmade lace (42). His uncle was the naturalist Jacques Julien Houtou de Labillardière. Details about his childhood and education are sparse. In July 1817 he was "preparateur" (a post in the French universities) for Dulong's physics and chemistry classes in l'Ecole véterinaire d'Alfort (43). Later he held the same post in the Collège de France in Paris with Thenard, with whom he worked from 1819 until 1821 (44). It is possible he was later forced to leave Paris and retire to his native Normandy for reasons of health (45). By 1825 he was in Rouen, where he had described his chlorometer to the academy on April 2, 1824 (18). On September 6, 1825 he was named a member of the "Académie de Medicine" in the Pharmacy section (46), but his dedication to continue chemistry teaching in Rouen is evident from his presentation of the colorimeter (22). His successor as Thénard's "preparateur, Lecanu, later wrote a memorial text to Labillardière upon his death in 1867.

As a chemist he worked on a great variety of problems, although he did not always successfully conclude his investigations. It is remarkable to note that Lecanu (45) once observed that Labillardière might have had the honor to codiscover quinine with Pelletier and Caventou, had he continued along a line of investigation carried out in the course of a lesson given in the Collège de France. He later continued his investigations into essential oils of petroleum and natural camphor and his search for the essence of turpentine (47), work that was at the center of a great deal of controversy. There was also controversy concerning his paper on malic acid, which he said was identical to sorbic acid (48).

Labillardière made important technical contributions in the field of dyes. He designed a piece of apparatus we can consider to be the first colorimeter. From his work on dyes derived from rubber he devised a color he called "solitaire," which became important in the French fashion world and from which he realized some economic benefit (45).

Disillusioned over the constant controversies with other academic chemists, he found the industrial environment more attractive around 1827, when evidence of his activity as a scientific investigator seems to have disappeared. Toward the end of his life, he and his wife became interested in botany and entomology. He died in Alençon on January 12, 1867 (42).

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