Educación Química

Reflexión

Léon Aimé Claris Vignon

Jaime Wisniak[1]

Resumen

León Aimé Claris Vignon (1853-1925) fue un industrial y químico francés que investigó la química del manitán, manitol y sus derivados, y de la celulosa, oxicelulosa e hidrocelulosa. Junto con Philippe Barbier, estudiaron la síntesis de safraninas sustituidas. Vignon desarrolló un proceso simple y rápido para la síntesis de manitán, sus propiedades y derivados; con Barbier desarrollaron un método para sintetizar fenosafranina y sus homólogos, basado en la reacción entre amidobenceno con nitrobenceno, y con Dubois estudiaron los efectos fisiológicos de la p- y m-fenilendiamina. Vignon desarrolló métodos analíticos para determinar el CO2 como gas o en solución, acetona en metanol, ácido fosfórico en superfosfato, tanino en uvas y vino, y mercurio y cobre en cantidades diminutas.

Palabras clave: celulosa, manitol, oxicelulosa, p- y m-fenilendiamina, fenosafranina, safranina, tanino.

Abstract

Léo Aimé Claris Vignon (1853-1925) was a French industrialist and chemist who investigated the chemistry of mannitan, mannitol, and their derivatives, and of cellulose oxycellulose, and hydrocellulose. Together with Philippe Barbier, they studied the synthesis of substituted safranins. Vignon developed a simple and fast process for the synthesis of mannitan, its properties, and derivatives; with Barbier they developed a method for synthesizing phenosafranine and its homologues, based on the reaction between amidobenzene with nitrobenzene, and with Dubois they studied the physiological effects of p-and m-phenylenediamine. Vignon developed analytical methods for determining CO2 as gas or in solution, acetone in methanol, phosphoric acid in superphosphate, tannin in grapes and wine, and mercury and copper in minute amounts.

Keywords : cellulose, mannitol, oxycellulose, p-and m-phenylenediamine, phenosafranine, safranin, tannin.

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[1] Ben-Gurion University of the Negev, Beer-Sheva, Israel.

Life and career (Anonymous, 2024; Martine & Raymond, 1024)

Léo Aimé Claris Vignon (1853-1925) was born in Sainte-Étienne (Loire, France) on August 11, 1850, the son of Antoine Vignon (1804-1894), a fabrics merchant, and Marie Olympe Octavie Mercier (1820-1876). Vignon took his basic education at the lycées of Saint-Étienne and Lyon and after receiving his diplomas of baccalauréat en lettres et en sciences at Lyon (1868), and Licence ès-sciences physiques at the Université de Lyon (1870), he served as a volunteer during the Franco-Prussian War (1870-1871). At the end of the war, he began doctoral studies at the University of Lyon, under the guidance of Adrien-Joseph-Jean Loir (1816-1899), and completed them at the Sorbonne in Paris, in 1874, after successfully defending a thesis about mannitol and its derivatives (Vignon, 1874b). Between 1874 and 1875 he dedicated himself mainly to industrial activities in the textile area but found time to carry extensive research in a variety of scientific subjects, as well as serve in various academic positions. Thus, in 1886 he was appointed sub-director of the laboratory of chemical industry at the Faculty of Sciences of Lyon; in 1891 lecturer of industrial chemistry at the same institution, and in 1896, promoted to professor of chemistry applied to the industry and agriculture, and Directeur of the School of Industrial Chemistry and of the Agronomical Station. In 1898 he served as director of the Martinière Lyon. Vignon was awarded the 1891 Leblanc Prize of the Société de Chimique de Paris and the1892 Prize of Chemical Arts by the Société d'Encouragement pour l'Industrie Nationale. Vignon was one of the founding members of the Société des Grands Concerts and creator and founder of a symphonic orchestra; he was member of the Société Lyonnaise de Sauvetage de l'Enfance; of the Académie des Sciences, Belles-lettres et Arts de Lyon (1896-1923), of the Société d'Agriculture de Lyon, etc. He was appointed Officier de la Académie (1892) and Officier de l'Instruction Publique (1898) (national order bestowed by the French Republic on distinguished academics and teachers and for valuable service to universities, education, and science), and Chevalier de la Légion d'Honneur (1898).

Scientific contribution

Vignon wrote about 60 papers and books (i.e., Vignon, 1891a, 1893) about his research activities in organic, inorganic, and analytical chemistry, toxicology, sugars, thermochemistry, etc. In addition, he was granted seven patents covering the manufacture of textile dyes (i.e., Vignon, 1884, 1885). As customary for candidates to the Académie des Sciences, he prepared a booklet describing his research activities and achievements (Vignon, 1893a). In addition to the few subjects presented below, Vignon determined thermochemical data about several organic compounds (Vignon, 1888ab, 1889, 1890ac); studied the chemistry of tin (Vignon, 1889bc) and the theory of textile tincture (Vignon, 1891bc); determined the fusion point of many compounds and their mixtures (Vignon, 1891cd); prepared fibroin and determined its properties (Vignon, 1892bc); etc.

Mannitol and derivatives

Mannitan (1,4-anhydro-D-mannitol, C6H12O5) was discovered by Marcelin Berthelot (1827-1907) in 1856 during his study of the decomposition of mannitol compounds by water, alcohol, acids, and alkalis. Mannitan could be easily separated from others by taking advantage of its neutrality, its solubility in water and absolute alcohol, and insolubility in ether (Berthelot, 1856). For example, it could be prepared by heating mannitol stearate with water at 240 oC for several hours in a sealed tube, followed by evaporation of the resulting liquor, extraction of the residue with absolute alcohol, and evaporation of the alcoholic extract (Berthelot, 1856). Berthelot described it as a neutral syrupy substance, containing, by weight, 44.5% carbon, 7.2% hydrogen, and 48.3% oxygen (by difference), corresponding to the formula C6H6O5 (Berthelot is using the old values of atomic masses). Heated strongly in contact with air it released a caramel odor, burning with a reddish flame, and leaving a carbonaceous residue. Left in contact with air, it deliquesced and after a long time regenerated the crystals of mannitol (Berthelot, 1856).

According to Vignon, all the methods available for preparing mannitan were lengthy and of low yield (Vignon, 1873a). After much work, he was able to develop a simple and fast process that allow preparing rapidly large amounts of mannitan: it was enough to heat mannitol with one-half its weight of concentrated sulfuric acid at 120o-130 oC. The mixture, which turned liquid within one hour, was neutralized with barium carbonate, while keeping the reaction temperature, and then left to cool. The cooled liquid was extracted with absolute alcohol, filtered, and the filtrate evaporated on a water bath. The residue was extracted with water, filtered over animal carbon, and dried at 100 oC. The resulting material was neutral, dextrorotatory, deliquescent, non-fermentable, reduced Fehling's liquor, and turned to mannitol with baryte water. The reaction could be easily followed by taking advantage of the optical activity of mannitan (Vignon, 1873a).

In 1866, Adrien Joseph Loir (1816-1899) reported that aqueous solutions of hexanitromannitol were dextrorotatory although mannitol was thought to be optical inactive (see above) (Loir, 1866-1867). Afterwards, this characteristic was shown to be present in most derivatives of mannitol. Vignon speculated that the possible reason for this discrepancy was due to mannitol having a very low rotatory power, which perhaps could be increased by adding boric acid to its solutions, as suggested by Jean Baptist Biot (1774-1862) (Biot, 1844; Vignon, 1873b). For this purpose, he used mannitol and boric acid, carefully purified by repeated crystallizations, and verifying that separate solutions of these substances did not deviate the plane of polarized light. Vignon's assumption was found to be true: ternary aqueous solutions of both components showed optical activity. Not only that, using borax instead of boric acid resulted in a larger manifestation of optical activity. In other words, mannitol was optically active, and the only role of boric acid and borax was to increase the asymmetry present initially in the carbohydrate (Vignon, 1873b).

Vignon added that the rotatory power [α] of each member of a series of mannito-boracic solutions, having a constant ratio (n) of the weight of mannite to the weight of water, should be related to the weight β of borax contained in the unit of weight of the same solution by the relation proposed by Biot (Biot, 1844):

$$[\alpha] = A + B\beta / (\beta + C)$$

where the three coefficients A, B, and C could be determined by means of three preliminary experiments (Vignon, 1874a). Vignon found that the rotatory power of a series of solutions having $n = 6.335136$ and β from 0.01396 to 0.0969484, varied from 2.5097° to 16.4638°, leading to the values $A = 0.82550$, $B = -39.797682$, and $C = - 0.344687$. In the case of no borax, that is, $\beta = 0$, the above equation yielded $[\alpha] = A = 0.8250$, which should be considered the rotary power of the mannitol, for the proportion of water specific to the series.

Vignon understood that although his result was not entirely correct, it was probably very close to the true value, since Biot had shown that the coefficient A, for the case of tartaric acid, substantially represented the rotatory power of this acid, Consequently, mannitol dissolved in water was a dextrorotatory body of very weak rotary power (Vignon, 1874a).

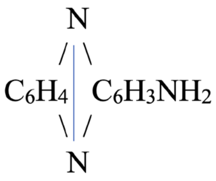
As mentioned before, all the above work became part of the doctoral thesis of Vignon (Vignon, 1874b) and the pertinent publication in a scientific journal (Vignon, 1874c). This thesis included an historical review of mannitol and its properties, since its discovery by Joseph Louis Proust (1754-1826) in the manna exudated by several species of ash trees (Proust, 1806); a very detailed chapter about the determination of the rotatory power of mannitol, mannitan, its preparation, properties, and derivatives, the reaction of mannitol with water under different conditions, etc.

Safranines

Philippe Barbier (1848-1922) and Vignon developed a new method to synthesize substituted saffranines, such as phenosafranine, by the reaction of p-phenylenediamine, or dimethyl p-phenylenediamine with aniline or p-toluidine. To them, safranines were compounds that arose from the condensation of one molecule of paradiamine with two molecules of an aromatic monoamine, with elimination of four molecules of hydrogen, under the influence of oxidants. The diamine used could be as such or asymmetrically substituted, and one of the monoamine molecules had to be primary and the second, secondary or tertiary (Barbier & Vignon, 1887ab).

In their first experiment, Barbier and Vignon tried to prepare an indamine by reacting one molecule of p-phenylenediamine with one of aniline and noticed the formation of a very unstable blue compound, which they separated by repeated washing with salty water, followed by filtration. This compound slowly transformed at room temperature, and instantaneously at 100 °C, into a red substance, which several tests proved it was phenosafranin. Repeating the experiment with two molecules of aniline for one molecule of p-phenylenediamine, resulted in a substantial increase in yield (Barbier & Vignon, 1887a).

The high instability of the blue compound did not allow its purification and analysis. Nevertheless, Barbier and Vignon were able to study some of its reactions, for example, hydrogenation with a mixture of zinc and dilute HCl, at room temperature. This reaction split into the compound into aniline, which remained in solution, and a new substance, precipitable by salty water, which behaved like a leucobase. In contact with air, this base oxidized slowly into another base whose hydrochloride $C_{12}H_9N_3.HCl$ crystallized in fine red needles and dissolved in water yielding a red solution, less intense than that of phenosafranin. Barbier and Vignon found that that the chemical properties of this new base were like those of diamidophenazine and dimethylamidophenazine, hence they proposed the formula (Barbier & Vignon, 1887a):



$$C_6H_4\begin{array}{c} N \\ / \,|\, \backslash \\ \\ \backslash \,|\, / \\ N \end{array}C_6H_3NH_2$$

Barbier and Vignon postulated that the changes they had observed could be explained by a four-step sequence: (1) Formation of the blue compound, (2) it's transformation in safranine, (3) it's splitting under the influence of nascent hydrogen and slow oxidation of the leucoamidophenazine to regenerate amidophenazine, and (4) formation of phenosafranine by oxidation of the leucoamidophenazine in the presence of aniline (Barbier & Vignon, 1887a).

Barbier and Vignon concluded that their results represented a new way to prepare substituted safranins, based on the use of nitrosodimethylaniline, and of phenazines and amidophenazines, starting from aromatic secondary monoamines, such as diphenylamine and dicresylamine (Barbier & Vignon, 1877a).

According to Barbier and Vignon, it was known that the reaction of nitrated derivatives of aromatic tertiary monoamines with primary monoamines of the same series, gave colored products. Their previous findings with substituted safranines led them to study this reaction in detail (Barbier & Vignon, 1877b).

Their first experiments were carried with p-nitrosodimethylaniline and aniline, in various solvents (i.e., water, glacial acetic acid, and alcohol of 92%). With the first two solvents, the reaction was nil at ordinary temperature and very lively and almost uncontrollable, at around 80 °C. Using alcohol of 92% and a reflux condenser, the rate of reaction controlled itself, and the heat released maintained a temperature varying between 78° and 80 °C during the first 15 to 20 minutes. In this situation, further heating of an equimolar mixture of p-nitrosodimethylaniline hydrochloride and aniline, dissolved in eight times its weight of ethanol at 92o, resulted in a liquid initially yellow, then brown, and finally bright purplish red (Barbier & Vignon, 1877b).

Upon cooling, the final mixture precipitated a solid substance, which after washing with a diluted solution of HCl, followed by repeated crystallization from boiling toluene, delivered a purified product composed of shiny and flaky brown crystals. These crystals were sparingly soluble in water and diluted acids, very soluble in concentrated acids and melted partially at 218°-220 °C, without releasing vapors. Elemental analysis indicated that they contained, by weight, 71.6% of carbon, 7.61% hydrogen, and 20.79% nitrogen (by difference), corresponding to the formula $C_{16}H_{20}N_4$. Reduced by zinc and diluted sulfuric acid, this compound converted almost quantitatively into dimethyl p-phenylenediamine $C_6H_4NH_2,N(CH_3)_2$. All these results indicated that the initial material was tetramethyldiamidoazobenzene (Barbier & Vignon, 1877b).

The purple alcoholic solution, separated by filtration from the tetramethyldiamidoazobenzene, was evaporated to a viscous residue and then extracted with boiling water and separated into a colored matter found to be dimethylphenosafranine. In other words, the reaction of p-nitrosodimethylaniline hydrochloride with aniline in alcoholic solution, produced tetramethylodiamidoazobenzene and dimethylphenosafranine (Barbier & Vignon, 1877b).

In a second part, Barbier and Vignon described another method for producing phenosafranine and its homologues, based on the reaction of amidoazobenzol with nitrobenzene in the presence of a reducing agent capable of releasing H2 (Barbier & Vignon, 1877b). Basically, the reaction consisted in heating in an oil bath at 180 °C, a mixture formed of one molecule of amidoazobenzol hydrochloride, nitrobenzene, iron, and HCl. The mixture, faintly brownish at first, gradually took on a purplish red color, becoming darker and darker and releasing water vapor entraining a little nitrobenzene. The final product was mixed with water and steam distilled to eliminate the excess nitrobenzene. Treatment of the product with ammonia, salty water, etc. left a precipitate of phenosafranine, which was purified with sodium chloride and boiling water. The pure red solid was very soluble in boiling water, in alcohol, and in concentrated sulfuric acid. Barbier and Vignon found that the reaction of the amidoazo derivative of o-toluidine with nitrobenzene, also provided a safranin (Barbier & Vignon, 1877b).

The pharmacologist Rafael Dubois (1849-1929) and Vignon studied in detail the physiological effect of p- and m-phenylenediamine. These two bases were particularly interesting because they had the same elementary composition and molecular weight, both had a double basic function, and presented with leucomaines and ptomaines a remarkable similarity of chemical functions. They constituted a typical example of the special isomerism of disubstituted derivatives of benzene (Dubois & Vignon, 1888a).

M-phenylene diamine, $1,3\text{-}C_6H_4(NH_2)_2$, was prepared by reducing pure m-dinitrobenzene with tin and HCl. After complete reduction, the tin was precipitated by hydrogen sulfide, the liquor made alkaline and then extracted with ether. Vacuum evaporation of the ethereal extract left a residue of impure m-phenylenediamine, which was purified by distillation in a stream of hydrogen and crystallization from benzene. M-phenylene melted at 63 oC. P-phenylenediamine, $1,4\text{-}C_6H_4(NH_2)_2$, was prepared in the same manner by reducing pure p-nitroaniline. The ethereal extract was purified by repeated distillation, followed by sublimation in a stream of hydrogen. It melted at 140 °C and distilled at 267o-268 °C (Dubois & Vignon, 1888a).

Dubois and Vignon found that both poisons presented common symptoms. Treating dogs with 0.1 g per kilogram of animal resulted in salivation, vomiting, diarrhea, emission of urine copious at times, then death in a coma, after two to three hours with p-phenylenediamine and twelve to fifteen hours with m-phenylenediamine. These two bases were gradually oxidized during their absorption by the body, generating brownish products, which gave the blood and the tissues a dark coloration. In addition, each one had some unique and specific properties. For example, m-phenylenediamine produced all the symptoms of an intense flu in dogs, the animal, seized with a violent catarrhal inflammation of the mucous membrane in the nose, sneezed constantly; experimented a very characteristic hoarse cough, and finally died in a comatose state like that developed by certain infectious diseases. P-phenylenediamine acted particularly on the eyes. Injected subcutaneously in any point of the body it promptly generated an extraordinary bulging or protruding of the eyeballs. Eventually, the lacrimal glands became covered with a brown pigment, making them look like tumors deposited on the surface of the eye (Dubois & Vignon, 1888a).

This report was reproduced in another medical journal, giving a much more detailed description of all the symptoms and effects of both compounds, including the results of the autopsy examination (Dubois & Vignon, 1888b).

Cellulose, oxycellulose, and hydrocellulose

Vignon carried extensive research on cellulose, oxycellulose, and their derivatives (Vignon, 1897, 1898bcf, 1900). Oxycellulose was discovered in 1883 by George Witz (1837-1885) during a study of the action of calcium chloride on cotton during bleaching operations, (Witz, 1883). So far, little information was available about its physical and chemical properties. Vignon obtained oxycellulose from pure cellulose prepared by purification of cotton. The physically clean cellulose was treated with successive baths of diluted sodium carbonate, concentrated HCl, and water at 100 oC, followed by washing with cold alcohol of 93o, and air drying (Vignon, 1897). Thirty grams of purified cellulose were oxidized by immersion for one hour, in a boiling bath containing 150 g of potassium chloride, 150 cm^3 of HCl, and 3 liters of water. During this period, the liquid turned yellow, chlorine compounds were released, and a white powder deposited. This powder was separated by decantation and washed repeatedly with hot water until no acid reaction was observed. The process was terminated by washing with alcohol and drying in the open air, on filter paper and porous brick. Microscopic examination indicated that oxycellulose was made up of very short filaments, which turned yellow at 100 oC, was insoluble in neutral reagents, was colored blue by iodine and sulfuric acid, and strongly reduced Fehling's liquor, showing the presence of an aldehyde function. Elemental analysis indicated that it contained, by weight, 43.15% carbon, 5.97% hydrogen, and 50.65% oxygen (Vignon, 1897).

Vignon found that the heat of combustion of oxycellulose varied between 4124 to 4133 cal/g compared with 4190 to 4224 cal/g for cellulose. The heats of immersion in a bath containing 500 cm^3 KOH normal at 13 °C, were 2.30 cal/100 g for oxycellulose and 0.74 cal/100 g for cellulose, indicating that the oxidation process had increased the acid character of the product. Comparison of the absorption of the basic colors safranin and methylene blue indicated that the respective weights were 0.007 and 0.006 g for oxycellulose and 0.000 and 0.002 for cellulose. Treatment of oxycellulose with aqueous KOH produced a golden liquor, which reduced the Fehling solution, did not reduce Schiff's reagent (prepared with fuchsin and SO2), and with HCl, lost its color and gave a white precipitate (Vignon, 1897).

Vignon prepared oxycelluloses by three different methods: (1) In an acid medium, with potassium chloride, HCl, and water. Yield: 73.2%; (2) in an alkaline medium, with sodium hypochlorite, sodium hydroxide, and water. Yield: 16.5%; and (3) with chromic acid, sulfuric acid, and water. Yield: 85%. He also reported the formation of the respective osazones (Vignon, 1899).

Vignon also demonstrated that the celluloses originating from cotton, hemp, flax, and ramie gave sensibly the same oxidation products (Vignon, 1900).

Vignon studied in more detail the action of KOH on oxynitrocellulose (Vignon, 1898f). For this purpose, he mixed 5 g of the oxynitrocellulose prepared as shown above, with 50 g of an aqueous solution of KOH (relative density 1.160) and noticed that the temperature rose 20o to 45 °C while, at the same time, the oxynitrocellulose dissolved with slight evolution of gas, giving a brown liquor. The resulting solution was cooled, neutralized with acetic acid at 0 °C, and then treated with a stream of H2S at room temperature. This resulted in the release of oxygenated compounds of nitrogen and deposition of sulfur. The brown filtrate was degassed by heating, cooled, and then mixed with a solution of acetic acid, phenylhydrazine, and water. The crystalline precipitate was filtered, and washed with pure water (Vignon, 1898f).

Under the microscope, this precipitate was shown to be formed of light-yellow crystals, mixed with a brown amorphous and resinous substance, which could be eliminated with cold benzene. The purified crystals were formed of small yellow prisms, melting at 204 oC. Elemental analysis indicated that they contained, by weight, 64.40% carbon, 5.40% hydrogen, 11.87% oxygen, and 19.33 nitrogen (total 101). The conditions of formation indicated that this substance had to be an osazone. Further analysis showed that it was the osazone of oxypyruvic acid. According to Vignon, the results of his experiments indicated that the action of an aqueous solution of KOH on oxynitrocellulose, resulted in the formation of oxypyruvic acid $CH_2OH\text{-}CO\text{-}COOH = C_3H_4O_4$ (sic) (Vignon, 1898f).

In a following paper, Vignon communicated the results of his study on the formation of furfural from cellulose, oxycellulose obtained by the oxidation of cellulose with water, HCl and potassium chlorate, and hydrocellulose prepared by the action of water, HCl, and tin chloride on cellulose (Vignon, 1898b).

These three modified celluloses were subjected to the action of boiling HCl of specific gravity 1.06, to the determine the formation of furfural according to the Tollens process. The furfural obtained was determined by distillation of the resulting liquor by transforming it with phenylhydrazine into its hydrazone. Vignon also carried this process with starch, cotton bleached with chlorine, and oxycellulose prepared by the action of chromic acid on cellulose. The amounts of furfural (%) obtained were as follows: Hydrocellulose, 0.854; oxycellulose, 2.113; reduced cellulose, 0.860; starch, 0.800, bleached cotton, 1.800; and chromic oxycellulose, 3.500. In every case, the formation of furfural was accompanied by formation of CO2 (Vignon, 1898b).

Ten grams of the three dry celluloses were also subject to nitration with a mixture of 150 cm^3 of 3 parts by weight sulfuric acid of relative density 1.841 and one part of nitric acid of density 1.50, for 24 hours at 10 oC. Substantially equal weights of product were obtained in all three cases (14-16 g). Nitrogen was assayed in these nitrated products in the form of NO (Vignon, 1898c).

The resulting nitrated products were flammable when stored in air; nitrated hydrocellulose and oxycellulose turned yellow and deteriorated while nitrocellulose was shown to be stable. Treatment with the Schiff reagent (fuchsin, sulfurous acid) showed that nitrated cellulose and hydrocellulose had weak aldehyde properties; those of nitrated oxycellulose were more accentuated but did not seem to have increased by nitration. The three substances reduced the boiling Fehling liquor and were attacked by a solution of KOH of relative density 1.35. Treatment with HCl (specific gravity 1.06) gave off large quantities of nitrous vapors; their distillate showed the formation of furfuraldehyde in small quantities. According to Vignon, these results indicated that that cellulose, in its transformation into hydro- and oxycellulose, had not undergone very considerable changes in the elementary structure of its initial chemical type (Vignon, 1898c).

Analytical chemistry

Carbon dioxide

Vignon noticed that the color of a mixture of 50 cm^3 of limewater and 10 drops of a saturated alcoholic solution of pure phenolphthalein, disappeared promptly by the addition of a sufficient quantity of an aqueous solution of CO, free or combined with neutral calcium carbonate. This result led him to propose a new volumetric method for detecting CO_2, free or half-combined, dissolved in water, by neutralization by means of a standard solution of calcium hydroxide, using phenolphthalein as indicator (Vignon, 1887).

Basically, the process consisted in mixing 50 cm^3 of the water being tested with 0.05 cm^3 (10 drops) of a saturated alcoholic solution of phenolphthalein, and a small quantity of titrated limewater, until it turned pink in the presence of excess lime. This limiting color was compared with that of a liquor of the same composition as the water to be examined but completely deprived of CO_2. The comparison standard consisted of freshly distilled water or a portion of the water to be examined, which had been boiled beforehand for a sufficient time to expel all the CO_2, which it contained. This standard was mixed with phenolphthalein as the sample examined. Equal coloration indicates that both liquids contained the same quantities of free calcium hydroxide; the difference between the calcium hydroxide consumed for the water to be examined and that which served to color the standard obviously corresponded to the CO_2 sought, calculated as follows:

$$V_{CO2} = [(n)(T)(22)]/[(n')(37)(1.9774)] = 0.3(nT/n') \ cm^3$$

at 0 °C and 760 mmHg, where n is the number of cubic centimeters of limewater consumed for the water to be examined (minus the quantity used for the standard), n' the volume of water (in cubic centimeters) on which the dosage was carried out, and T the title of limewater, expressed in grams of calcium hydroxide per liter, Vignon added that the result was not affected by the presence of chlorides, sulfates and nitrates of calcium and magnesium (Vignon, 1887).

Vignon and Louis-Marius Meunier used the same arguments to develop an analytical method for determining the amount of CO_2 present in various gases (Vignon & Meunier, 1900). Basically, the experimental apparatus consisted in a flask connected with a calibrated burette, which could be opened and closed at will, and another tube and valve for letting gases out. The flask was filled with the gas tested and a titrated solution of limewater reddened with phenolphthalein gradually introduced. The limewater would retain a persistent pink color only after complete neutralization of the CO_2. The operation was made faster and more complete by adding a small amount of ethanol for facilitating the formation of insoluble calcium carbonate. The proportion of CO_2 was determined by the quantity of limewater used to obtain the red coloration, less the quantity absorbed for the coloration of the phenolphthalein (Vignon & Meunier, 1900).

Performance of the test required an alcoholic solution of 5 g of phenolphthalein in 100 cm^3 of ethyl alcohol at 93°, perfectly neutral and filtered; a saturated and titrated solution of calcium hydroxide containing 1.8 g $Ca(OH)_2$ per liter at a temperature of 15 °C; and ethanol of at 93°, neutral, having been degassed immediately before carrying out the determination. Vignon and Meunier illustrated the application of their procedure for the dosage of CO_2 in lighting gas and in a confined gas space and added that in a similar manner it could be applied to other gases such as gases of blast furnaces and of hearths, if they did not contain acid gases other than CO_2 (Vignon & Meunier, 1900).

Acetone in methanol

Vignon wrote that ethanol for industrial uses was usually denatured with crude methanol (methylene), containing 20 to 23% acetone. The quantitative analysis of this methanol was normally done using the method of Gustav Kraemer (1842-1924), based on the fact discovered by Adolf Lieben (1836-1914) that pure methanol did not yield iodoform in the presence of iodine and NaOH while acetone did it (Kraemer, 1880; Lieben, 1868; Vignon, 1890b). In the Kraemer method, 1 cm^3 of the methanol and acetone mixture were heated with 10 cm^3 of NaOH (2 normal) and 5 cm^3 of a 2-normal iodine solution and the resulting iodoform extracted with 10 cm^3 of alcohol-free ether. The solvent was eliminated by evaporation and the proportion of acetone calculated knowing that one molecule of acetone yielded one molecule of iodoform.

According to Vignon, his experience indicated that the Kraemer method gave reasonable results only with methanol containing very small amounts of acetone, well below the amounts present in methylene. For example, a synthetic mixture containing 21.5 g of acetone per 100 cm^3, mixed with the amount of iodine prescribed by Kraemer, indicated that it contained only 5.94 g of acetone. This figure augmented substantially using increasing amounts of iodine. In addition, reversing the order of addition of the reagents also led to a wrong result. According to Vignon, these anomalies could be easily understood inspecting the chemical reactions taking place in Lieben's procedure:

$$\mathrm{6I + 6KOH = 5KI + KIO3 + 3H2O} \qquad (1)$$

$$\mathrm{(CH3)2CO + 6I + 4KOH = CH3COOK + CHI3 + 3KI + 3H2O} \qquad (2)$$

Hence, Vignon proposed modifying Kraemer's method as follows: (a) 5 cm^3 of the methylene are dissolved in about 200 cm^3 of distilled water and water added to complete 250cm^3; (b) 5 cm^3 of this solution are put in a test tube of 100 cm^3 together with 10 cm^3 of NaOH (2 normal), and 5 cm^3 of an iodine solution iodine (2 normal); (c) the contents are stirred for some minutes and then extracted with 10 cm^3 of alcohol-free ether and the volume V noted; (d) a 5 cm^3 sample is evaporated under vacuum, leaving iodoform (p) as residue, and (e) the weight x of acetone in 100 cm^3 of the mixture is calculated as follows (Vignon, 1890b):

$$x = (1000)(p)(V)(58)/(5)(394) = 29.44(p)(V)$$

(True masses: acetone =58.08 and iodine 126.90).

In a following publication, Vignon indicated that the above method as such, was not applicable, a priori, in the presence of ethanol; to do so, it was necessary to take certain precautions (Vignon, 1891b). His arguments were since depending on the environment, it could well be that one of the above equations (1) and (2), could predominate over the other, and the whole process require different amounts of iodine. In addition, the presence of ethanol exerted a remarkable influence on the direction of the reaction. Ethanol alone did not give iodoform, mixed with acetone it opposed the formation of iodoform and tended to make reaction (1) predominate. Vignon illustrated this fact with a practical result: 5 cm^3 of a mixture of acetone and distilled water, treated with iodine and NaOH, gave an amount of iodoform corresponding to 55.34 g of acetone per 100 cm^3. For a mixture of equal volumes of acetone and absolute alcohol, the result was 28.54 g. In addition, the presence of aldehydes promoted the formation of iodoform (Vignon, 1891b).

Accordingly, Vignon concluded that the correct use of his method required that the sample be first cleared of aldehydes and then treated with a large excess of iodine. The test indicated above should be repeated with 20 cm^3 of NaOH (2 normal) and 10 cm^3 of iodine. The dosage was definitive when these two tests gave the same answer (Vignon, 1891b).

Mercury

Vignon's study of the absorbent power of cotton on diluted solutions of mercuric chloride (Vignon, 1893b), led him to try to develop a method for the dosage of mercury at high dilution (Vignon, 1893c). He was aware that the determination of mercury by weighing its sulfide, was easily applicable to solutions of mercuric chloride diluted to the thousandths. Basically, this was done, for example, by adding to 50 cm^3 of solution of HgCl2 to the thousandth, 5 cm^3 of pure concentrated HCl and 10 cm^3 of a saturated and clear solution of hydrogen sulfide. The resulting yellow precipitate turned quickly black and was filtered through a filter weighed beforehand with a milligram scale. The precipitate was washed, dried, and weighed. As a comparative standard, it was useful to repeat this operation with a mixture of 50 cm^3 of distilled water, 5 cm^3 of HCl, and 10 cm^3 of H2S (Vignon, 1893c).

According to Vignon, this weighing procedure could be carried, with some relative certainty, also to dosage the mercury in solutions of sublimate to ten-thousandth only by operating at least on 500 cm^3 of liquor, with the corresponding possible errors.

After much testing, he was able to develop a colorimetric method based on the intensity of the brown tint given by the sulfide of mercury HgS which, under certain conditions, remained dissolved. For this purpose, he prepared a solution containing 1/10000 parts of $HgCl_2$ (10 g $HgCl_2$/liter, solution A) and diluted it progressively, adding to each step, 10 cm^3 of H_2S and observing the resulting intensity of the coloration, as follows:

			Dilution in 1/1000a
1.	100 cm^3	A + 0 cm^3 distilled water	a = 11
2.	50	50	22
3.	40	60	27
4.	30	70	37
5.	20	80	55
6.	10	90	111
7.	5	95	200
8.	0	100	0

The concentration of the test solution was determined by its relative coloration (Vignon, 1893c).

Phosphoric acid in superphosphate

According to Vignon, there were three main procedures for determining the amounts of soluble phosphates present in superphosphates and in chemical fertilizers; (1) determination of phosphoric acid soluble in water; (2) determination of phosphoric acid soluble in water and of phosphoric acid soluble in citrate of ammonia, combined; and (3) the separate determination of the phosphoric acid soluble in water and of the phosphoric acid soluble in citrate of ammonia. These procedures were carried on in strict observance of the instructions of the Committee of Agronomic Stations and Agricultural Laboratories (Vignon, 1898a).

Vignon carried on several experiments under different conditions, to determine the validity of these tests and determine their advantages and disadvantages. He concluded that instead of assaying separately the phosphoric acid soluble in water and the phosphoric acid soluble in citrate, it was better to directly assay the phosphoric acid soluble in water, together the phosphoric acid soluble in water and citrate, and determine by difference phosphoric acid soluble in citrate (1898a).

In 1898, Henri Lasne reported that it was possible to determine the amount of phosphoric acid soluble in citrate present in fertilizers, very accurately, even when present in very small amounts, contrary to the opinion of Vignon (Lasne, 1898). Vignon replied that he did not negate Lasne's claim but that in practice there were important differences in the rate of integral precipitation of phosphoric acid, according as if this acid was present in considerable quantities. Agricultural laboratories sometimes had to conduct fast analysis and in large amounts, hence it was very possible that this inconvenience would lead to a mistaken answer. Vignon modification would avoid this possibility (Vignon, 1898d).

Tannin

In 1898 Vignon described a new method he had developed for dosing tannin in aqueous solutions, because tannin, to the exclusion of the other bodies which usually accompanied it (gallic acid, glucose, etc.), was easily and completely absorbed by scoured silk. Hence, it was enough to keep the silk-tannin mixture dissolved for four to five hours, at 50 oC, and use the silk in great excess compared to the tannin (Vignon, 1898e).

According to Vignon, the dissolved tannin could be determined by the following methods: (a) by direct weighing, by determining the difference in the absolute weights of the silk before and after absorption; (b) by difference, by weighing the extract at 110 °C of the tannin solution before and after absorption by the silk; and (c) by difference, by titrating with potassium permanganate, before and after the action of the silk, the tannin solution with the addition of indigo carmine, using the rule that 1 cm3 of potassium permanganate solution at 3.164 g per liter $K_2Mn_2O_7/100$ corresponded to 0.004155 of pure tannin. According to Vignon, process (a) was long, complicated, and lacked accuracy. Process (b) was very simple and quick and gave sufficient results for practice. Process (c) was the most correct (Vignon, 1898e).

According to Vignon, scoured silk, the basis material for carrying his test, was easily accessible in a high state of purity and homogeneity, it was regular, unalterable, and easy to weigh and handle. These properties were not present in the pertinent ingredients used in standard tests: Violin strings required quite a long preparation; skin powders were irregular, yielding soluble organic matter to water and did not present any guarantee. Absorption by silk took five hours at 50 oC, while ropes and skin powder could only be used cold and for about thirty hours. Finally, the coloring of the silk, after absorption, made it possible to compare the degree of coloring of the tannin: a very useful sign for dyeing and tannery (Vignon, 1898e).

Copper and mercury in wine products

Vignon and Etienne Barrillot (1872-1938) wrote that various metallic solutions were used to combat parasitic diseases of the vine, so it was of practical interest to know how much of these metals were present in the grapes, wines, lees, and marc. For this purpose, they had developed an analytical procedure, which allowed detecting very small amounts of both metals (Vignon & Barrillot, 1899). Basically, the method involved the following steps:

1. The grapes, the marcs, and lees were first washed with distilled water to eliminate the soluble metallic combinations. The resulting liquid was identified as (a).
2. The remaining material was washed with a 10% aqueous solution of aqua regia, which oxidized and solubilized the remaining the metallic combinations. The resulting liquid was identified as (b).

3. The wine and liquids (a) and (b) were acidified and then precipitated with a stream of hydrogen sulfide.
4. The pertinent sulfides of copper and mercury were separated by filtration and treated with boiling nitric acid. This step dissolved the copper sulfide, which could then be determined electrolytically.
5. The precipitate, freed from copper sulfide, was treated with aqua regia, which dissolved the mercury sulfide. This mercury was determined by the colorimetry method developed by Vignon (Vignon, 1893c)

Vignon and Barrillot stated that their method allowed copper and mercury in present in a wine to less than 1 milligram per liter (Vignon & Barrillot, 1899).

Vignon and Barrillot described in detail the preparation of all the reagents needed for carrying on the analysis, and the pertinent experimental procedures (Vignon & Barrillot, 1899).

References

Anonymous. (2024). France. Archives Nationales. Base Léonore, Dossiers Nominatifs des Personnes Nommées ou Promues dans l'Ordre de la Légion d'Honneur.

Barbier, P., & Vignon, L. (1877a). Recherches sur la Phénosafranine. Bulletin de la Société Chimique, 48, 338-342.

Barbier, P., & Vignon, L. (1877b). Sur un Nouveau Mode de Formation des Safranines Substituées. Comptes Rendus, 105, 670-672, 939-941.Berthelot, M. (1856). Sur les Combinaisons Neutres des Matières Sucrés avec les Acides. Annales de Chimie et de Physique [3], 47, 297-354.

Biot, J. B. (1844). Sur l'Emploi de la Lumière Polarisée pour Étudier Diverses Questions de Mécanique Chimique. Annales de Chimie et de Physique [3], 11, 82-112.

Dubois, R., & Vignon, L. (1888a). Sur l'Action Physiologique de la Para- et de la Métaphénylène Diamine. Comptes Rendus, 107, 533-535.

Dubois, R., & Vignon, L. (1888b). Étude Préliminaire de l'Action Physiologique de la Para- et de la Métaphénylène Diamine. Archives de Physiologie, 2, 255-260.

Kraemer, G. (1880). Über die Quantitative Bestimmung des Acetons im Methylalkohol. Berichte der Chemischen Gesellschaft Berlin, 13, 1000-1005.

Lasne, H. (1898). Sur le Dosage de l'Acide Phosphorique. Comptes Rendus, 127, 62-64.

Lieben, A. (1868). Di un Metodo per Scoprire l'Alcoole Mediante la sua Trasformazione en Iodoformio. Atti dell'Accademia delle Scienze di Torino, 4, 565-571.

Loir, A. (1866-1867). Sur le Pouvoir Rotatoire de la Mannite et ses Dérivés. Mémoires de l'Académie des Sciences de Lyon, 22, 157-158.

Martine, F., & Raymond, R. (2024). Vignon, Léo. In Dictionnaire des Membres de la Société Linnéenne de Lyon et des Sociétés Botanique de Lyon et d'Anthropologie Réunies (pp. 1729-1793). http://www.lineenne-lyon.org/depot6/6-11786.pdf

Proust, J. L. (1806). Mémoire sur le Sucre de Raisin. Annales de Chimie, 57, 131-174, 225-272.

Vignon, L. (1873a). De la Mannitane. Comptes Rendus de l'Association Française pour l'Avancement des Sciences, 2, 310-312.

Vignon, L. (1873b). Du Pouvoir Rotatoire de la Mannite. Comptes Rendus, 77, 1191-1192.

Vignon, L. (1874a). De l'Action de Systèmes Ternaires Définis, Formés de Mannite, de Borax et d'Eau, sur la Lumière Polarisée. Du Pouvoir Rotatoire de la Mannite. Comptes Rendus, 78, 148-149.

Vignon, L. (1874b). Recherches sur la Mannite. Thèses présentées à la Faculté des Sciences de Paris pour obtenir le grade de docteur ès sciences physiques. Gauthier-Villars.

Vignon, L. (1874c). Recherches sur la Mannite. Annales de Chimie et de Physique [5], 2, 433-473.

Vignon, L. (1887). Sur une Nouvelle Méthode de Dosage de l'Acide Carbonique Dissous. Comptes Rendus, 105, 1122-1124.

Vignon, L. (1888a). Thermochimie des Composés Diazoïques. Comptes Rendus, 106, 1162-1165.

Vignon, L. (1888b). Chaleur de Combinaison des Monoamines Primaires, Secondaires et Tertiaires Aromatiques avec les Acides. Comptes Rendus, 106, 1722-1724.

Vignon, L. (1889a). Formation Thermique des Sels de Phénylènes Diamines Diazoïques. Recherches sur la Paraphénylène Diamine. Comptes Rendus, 106, 1671-1674, 1757; Comptes Rendus, 109, 455-479.

Vignon, L. (1889b). Sur l'Étain. Comptes Rendus, 107, 734-737.

Vignon, L. (1889c). Action de l'Eau sur le Chlorure Stannique. Comptes Rendus, 109, 372-375.

Vignon, L. (1890a). Recherches Thermochimiques sur la Soie. Comptes Rendus, 110, 286-289.

Vignon, L. (1890b). Dosage de l'Acétone dans l'Alcool Méthylique et dans les Méthylènes de Dénaturation. Comptes Rendus, 110, 534-536; Bulletin de la Société Chimique, 3, 595-598.

Vignon, L. (1890c). Recherches Thermochimiques sur les Fibres Textiles. Comptes Rendus, 110, 909-910.

Vignon, L. (1891a). Recherches sur la Soie. Baillière.

Vignon, L. (1891b). Dosage de l'Acétone dans les Alcools Dénaturés. Comptes Rendus, 112, 873-875.

Vignon, L. (1891c). La Teinture du Coton. Comptes Rendus, 112, 487-489.

Vignon, L. (1891d). Sur la Théorie des Phénomènes de Teinture. Comptes Rendus, 112, 623-624.

Vignon, L. (1892a). Nouvelles Recherches sur la Soie. 2e série. Rey.

Vignon, L. (1892b). Le Pouvoir Rotatoire de la Fibroin. Comptes Rendus, 115, 442-444.

Vignon, L. (1892c). Sur la Préparation et les Propriétés de la Fibroin. Comptes Rendus, 115, 613-615.

Vignon, L. (1893a). Résumé Analytique des Publications de Léo Vignon, Maître de Conférences à la Faculté des Sciences de Lyon. Storck.

Vignon, L. (1893b). Action Absorbante du Coton sur les Solutions Étendues de Sublimé. Comptes Rendus, 116, 517-519.

Vignon, L. (1893c). Dosage du Mercure dans les Solutions Étendues de Sublimé. Comptes Rendus, 116, 584-586.

Vignon, L. (1884). Sulpho-Alpha-Naphthol Coloring Compound. USP310155A, granted 30.12.1884.

Vignon, L. (1885). Manufacture of Coloring Matter from Alpha-Naphthol and Dinitro-Naphthol. USP324615A, granted 18.08.1885.

Vignon, L. (1897). Sur l'Oxycellulose. Comptes Rendus, 125, 448-450.

Vignon, L. (1898a). Dosage de l'Acide Phosphorique dans les Superphosphates. Comptes Rendus, 126, 1522-1523.

Vignon, L. (1898b). Formation du Furfurol par la Cellulose et ses Dérivés Oxy et Hydro. Comptes Rendus, 126, 1355-1358.

Vignon, L. (1898c). Nitration de la Cellulose et ses Dérivés Hydro et Oxy. Comptes Rendus, 126, 1658-1661.

Vignon, L. (1898d). Dosage de l'Acide Phosphorique. Comptes Rendus, 127, 191.

Vignon, L. (1898e). Dosage du Tannin. Comptes Rendus, 127, 369-372, 456.

Vignon, L. (1898f). Action de la Potasse sur l'Oxycellulose. Comptes Rendus, 127, 872-874.

Vignon, L. (1899). Oséinitrate de Nitrates. Comptes Rendus, 128, 248-251.

Vignon, L. (1900). Oxycelluloses du Coton, Lin, du Chanvre et de la Ramie. Comptes Rendus, 131, 558-560.

Vignon, L., & Barrillot, E. (1899). Dosage du Cuivre et du Mercure dans les Raisins, les Vins, les Lies et les Marcs. Comptes Rendus, 128, 613-615.

Vignon, L., & Meunier, L. (1900). Méthode Rapide de Dosage de l'Acide Carbonique dans Divers Gaz. Comptes Rendus, 130, 513-515.

Witz, G. (1883). Recherches sur Certain Altérations du Coton. Bulletin de la Société Industrielle de Rouen, 11, 169-232.

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