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JEAN-FRANÇOIS PERSOZ

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ABSTRACT

Jean-François Persoz (1805-1868) was a Swiss-French pharmacist and chemist who with Payen isolated the amylase of malt (the first enzyme isolated and studied) and with Biot showed that the inversion of sugar could be followed by means of circular polarization. He also studied the chemistry and preparation of complex metallic oxides, the solubility of salts, the composition of madder, the dyeing and printing of fabrics, arsenic poisoning, etc.

Keywords: circular polarization; dextrin; diastase; dyes; madder; metallic oxides; solubility; sugar inversion

RESUMEN

Jean-François Persoz (1805-1868) fue un farmacéutico suizo-francés que junto con Payen aislaron la amilasa de la malta (la primera enzima aislada y estudiada) y con Biot demostraron que era posible seguir la inversión del azúcar mediante la polarización circular. También investigó la química y preparación de óxidos complejos, la solubilidad de sales, la composición del madder, el teñido y la impresión de textiles, el envenenamiento con arsénico, etc.

Palabras clave: polarización circular; dextrina; diastasa; colorantes; rubia; óxidos metálicos; Solubilidad; inversión del azúcar.

INTRODUCCIÓN

Life and career

Jean François Persoz (1805-1868) (Figure 1), was born on September 6, 1805, in Cortaillod (canton of Neuchâtel, Switzerland), the son of Pierre Persoz (1760-1839), a book peddler, and Jeanne-Marguerite Richardet. His parents, of modest means, wanted him first to become a priest, then a merchant, but eventually accepted his desire to become a pharmacist. Thus he carried his apprenticeship in pharmacies in Neuchatel, Geneva, and Paris (1823). While in Paris he also attended the chemistry courses given by Pierre-Louis Dulong (1785-1838) and Louis-Jacques Thenard (1777-1857) at the Collège de France. In 1825 Thenard hired him as his préparateur of the chemistry course and worked on the preparation of methane and the modifications of starch and gums by acids. In 1832 he became Thernard's substitute in his course on dyeing and printing. In 1833 he was awarded the degree of docteur ès sciences from the Faculty of Sciences of Paris after successfully defending a thesis about circular polarization, a technique that allowed differentiating between organic substances having identical appearance. In 1833 Persoz was appointed professor of chemistry at Strasburg, replacing Yves Marie Branthôme (1763-1832). During his tenure he reorganized the École Supérieure de Pharmacie and was its first director (1835-1852). In 1850 he served as substitute of Jean-Baptiste André Dumas (1800-1884) at the course of dyeing given by the latter at the Sorbonne. In 1852 he was appointed professor of chemistry of applied dyes at the Conservatoire des Arts et Métiers of Paris.

In 1830 Persoz married Aimée Verdan (1805-1896), from which he had three daughters (Rose Aimée, Sophie, and Fanny, and one son (Jules François).

Persoz was also member of several important organizations, among them Comité des Arts Chimiques de la Société d'Encouragement, Société Helvétique des Sciences Naturelles, Conseil d'Hygiène Publique et Salubrité, permanent commission of values, juror at the International Expositions of 1851, 1855, 1862, and 1867, etc. He also served as expert chemist in many criminal trials, and was also appointed officer of the Légion d'Honneur.

Jean-François Persoz died in Paris on December 9, 1868, after an appendicitis ailment, and was buried at the Père Lachaise cemetery.

Bernard Persoz, Persoz's great-grandson, has published an extensive collection of documents related to his great-grand father (Persoz, 1991).

Scientific work

Persoz wrote about 100 papers, booklets and books in the areas of inorganic and analytical chemistry, atomic masses, dyes and dyeing processes, fabric printing, enzymes, molecular theory, physiology, etc. He also wrote a short booklet describing his academic activities and his research and results (Persoz, 1834a). In addition to the subjects discussed below Persoz studied the use of chlorine as an antidote for HCN (Persoz and Nonat, 1830), a new theory about the molecular state of compound bodies (Persoz, 1835, 1836a, 1839), solubility in general and solubility of salts in particular (Persoz, 1836b), a new method for determining the composition of organic compounds (Persoz, 1840), duck fat (Persoz, 1844), dyeing and printing of fabrics (Persoz, 1846), the atomic mass of copper and structure of its oxides and salts (Persoz, 1849), the keeping of grains by means of lime (Persoz, 1857), a new procedure for separating phosphoric acid (Persoz, 1859), complex oxides (Persoz, 1861), preparation of ethyl nitrate (Persoz, 1862), etc.

Madder

Henri François Gaultier de Claubry (1792-1878) and Persoz wrote that several chemists had tried to extract and define the coloring matter contained in madder (*Rubia tinctorum*) (Gaultier de Claubry and Persoz, 1831); the most important work had been done by Charles Frédéric Kuhlmann (1803-1881) (Kuhlmann, 1823) and by Pierre-Jean Robiquet (1780-1840) and Jean Jacques Colin (1784-1865) (Robiquet and Colin, 1826). According to Kuhlmann the root of madder contained two dyes, one rose and the other red, malic acid, mucilage, gum, sugar, a bitter substance, a fragrant material, woody matter, and inorganic salts. The red dye was separated by precipitating with sulfuric acid the liquid obtained by cold maceration of the roots, followed by alcoholic extraction of the precipitate and evaporation. Robiquet and Colin believed that the product separated by Kuhlmann was not a pure principle and for this reason they developed a different extraction procedure (Robiquet and Colin, 1826). They mixed the roots with 3 or 4 parts of water and let them macerate for only 8 to 10 minutes at 15^0 to 20^0C. The resulting red-brown acid liquid gelled after some time, which depended on its concentration. The gel was separated, washed first with a little water and afterwards with a large amount of concentrated alcohol. The alcoholic extract was partially concentrated by distillation and then mixed with sulfuric acid. The resulting flaky precipitate was separated, washed, dried, and heated gently. The coloring principle sublimated and deposited as crystalline needles on the walls of the vessel. Robiquet and Collin named the *alizarin*, derived from the expression *alizari* used in commerce to designate the full root of madder.

The changes in color observed during the different purification stages led Robiquet and Colin to suspect the presence of a second coloring matter in the roots of madder. Eventually they separated it and named *purpurin* because of its red purple color (Robiquet and Colin, 1827).[8] Purpurin crystallized as needles, which were less soluble in aqueous alum than alizarin. This solution was colored dark red. Purpurin also dissolved in alkaline liquors to which it communicated a gooseberry tint, while alizarin colored it intense violet. Robiquet and Colin also reported that treatment of the roots with concentrated sulfuric acid carbonized all organic matter, except the coloring one, which apparently remained combined with the resulting carbon. They named the residue *sulfuric carbon*; this carbon treated with water produced a very acid colorless liquid. Repeated washing of sulfuric carbon with water until all the acidity was gone left a solid residue, which dissolved in aqueous alkali yielding a liquid capable of dyeing clothes in all the tones provided by madder itself (e.g. violet, red, black, etc.), depending on the nature of the mordant. Well-washed sulfuric carbon, treated with alum water, provided tinctures of a very pure color, which could be used for the preparation of lakes (Robiquet and Colin, 1827).

Gaultier de Claubry and Persoz did not believe that the coloring matters separated by Kuhlmann or by Robiquet and Colin were the true coloring principles of madder. They prepared the dyes according to their methods and observed they produced different colors when applied to cloths. After much experimenting they developed the following method for separating what they believed were the true colors of the root: The powdered roots were mixed with enough water to form a very thin mass and then 90 g of sulfuric acid were added for each kilo of the madder. The whole was now boiled directly with steam or over an open fire; the accompanying transformation of the gum into sugar allowed an easy readily extraction of the coloring matters. Addition of a mixture of tin oxide and KOH produced deep red liquor, which contained the two coloring principles. This liquid was neutralized by means of an acid which precipitated the two coloring matters; the precipitate was separated, carefully washed, and treated with alum water to separate the rose colored principle. The residue was dissolved in alcohol and distilled; the residual liquid was the red coloring principle, which crystallized by spontaneous evaporation. According to Gaultier de Claubry and Persoz the red coloring matter was of a brown red, slightly soluble in cold water and substantially more soluble in hot water, and soluble in alcohol and ether; by spontaneous evaporation it separated as crystalline needles. It was not altered by the weak acids and was readily soluble in the alkalis (Gaultier de Claubry and Persoz, 1831).

The rose-colored principle was separated from the aluminous liquid by addition of a slight excess of concentrated sulfuric or hydrochloric acid. The resulting orange red precipitate was washed, dissolved in alcohol, and evaporated, yielding the rose-colored principle. This principle, when in powder, was of a superb rose color; it was scarcely soluble in water, soluble in alcohol, ether and alkalis, and was not altered by diluted sulfuric acid. Treatment of the aqueous solutions with different reagents produced a variety of colored solutions (Gaultier de Claubry and Persoz, 1831).

Gaultier de Claubry and Persoz, 1831 believed that their method allowed the complete separation of the two dyes and explained why the results of Kulhmann and Robiquet and Colin yielded different colors.

Diastase

Many scientists had studied the nature of starch and its chemical reactions. For example, Sigismund Konstantin Kirchhoff (1764-1833) discovered that heating an aqueous solution of starch with mineral acids changed it into a gum, dextrin and raisin sugar, without the acids being modified by the reaction and without release of gas. Treating the resulting solution with alkali recovered all the acid employed (Kirchhoff, 1811). In 1818 Nicolas Théodore de Saussure (1767-1845) reported that starch at room temperature, in the presence of air and water, decomposed predominantly into crystallizable sugar (similar to the one generated when starch was treated with hot diluted sulfuric acid), a particular gum, and an intermediate substance between the gum and starch, which he named *amidine*. Amidine appeared to be a modified starch, insoluble in alcohol, slightly soluble in cold water and completely soluble in water above 63^0C; the solution was coagulated into a white paste by lead sub-acetate but not by lead acetate. The cold solution reacted with iodine producing a blue color, the same as starch. It was copiously precipitated by baryte water but not by limewater or an infusion of nutgalls; it dissolved in an aqueous solution of KOH and acids and alcohol precipitated it from this solution (Saussure, 1819).

François Vincent Raspail (1794-1878) showed that starch was not a homogeneous body but that each grain was a true vegetable organ shaped as transparent ovoid globules containing in its interior a gum-looking substance covered by a cortical envelop, unaltered by water or acids at ordinary temperatures and susceptible of long coloration by iodine. The internal substance was soluble in cold water, liquid even in its natural state; which by evaporation lost the power of being colored by iodine and possessing all the properties of gum. Raspail believed that the coloration by iodine was due to a volatile substance and not to the starch itself (Raspail, 1825).

Nicolas-Jean-Baptiste-Gaston Guibourt (1790-1867) made a microscopic examination of the starch grains and noticed that they were of all forms, changing from spherical to the small one, to triangular for the largest. The entire grain was colored by iodine without losing its transparence. Guibourt's experiments proved that the soluble and the insoluble parts of starch were equally colored by iodine and differed only in density and structure. The soluble part, after long boiling, was still colorable by iodine, proving that the coloration was not a volatile compound, as claimed by Raspail. Guibourt's results showed that a long boiling and evaporation to dryness did not remove the property of coloring iodine, that the soluble starch was not a gum, as claimed by Raspail, and that both the soluble and insoluble parts consisted of one immediate vegetable principle (Guibourt, 1829b).

According to Joseph Bienaimé Caventou (1795-1877) amidine was not a product of the spontaneous decomposition of starch because De Saussure had separated it by boiling the residue insoluble in water. The action of boiling was the one that had transformed starch into amidine (Caventou, 1826). Later on Michel Eugène Chevreul (1786-1889) suggested the names *amidine* for the soluble part and *amidin* for the insoluble one (Chevreul, 1829-1830).

Persoz and Jean-Baptiste Biot (1774-1862) studied the progressive reactions underwent by the starch grains under the action of diluted acids. For this purpose they heated a mixture of 500 g of potato starch, 120 g of sulfuric acid, and 1390 g of water and observed that about 85^0-95^0C it split into three parts (A, B, and C), which they separated, cooled, filtrated, and measured their rotatory power ($+66.083^0$, $+62.250^0$, and $+62.250^0$, respectively). The rotatory power solution of part B, heated to 100^0C, decreased to $+41.389^0$. Part C was afterwards heated with an additional amount of water until its volume returned to the original one and seen to transform into a different substance having a lower rotating power ($+25.750^0$). Equal volumes of the solutions were treated with equal volumes of alcohol; solutions A, B, and C produced a white slightly green pulverulent precipitate and D a dark red one. Biot and Persoz repeated the experiment using acid of different concentrations and temperatures and noticed that the rotation power was highly dependent on both factors: the rotation power increased with higher acid concentration and decreased when heating to a temperature below boiling. Higher temperatures led to a further decrease in the power (Biot and Persoz, 1833).

The next stage was the isolation of the different substances produced during the process and the study of their properties. These products were divided into three classes, depending if they were produced before, during, or after liquidity of the reaction mass. After a large number of operations Biot and Persoz were able to separate and purify a substance, which they named *dextrin*, having a rotation power substantially larger than that of sugar cane (in a ratio 200 to 84). Analysis indicated it contained only carbon, hydrogen, and oxygen. It was partly soluble in cold water and more soluble in hot water, the resulting neutral solution turned red under the action of iodine. The dissolved dextrin was precipitated by alcohol and lead sub-acetate. With beer yeast it produced alcohol and with acids it turned into sweet syrup. The latter result explained the strong change in rotation power caused by acids and heat. A solution of pure dextrin in water, abandoned to itself in the presence or absence of air, precipitated a white pulverulent solid, corresponding to modified dextrin. Summarizing, the progressive stages in the transformation of starch into sugar under the influence of a dilute acid consisted, first, in the tearing of the tegument, uncovering the internal substance (dextrin), and transformation of the latter into starch sugar (Biot and Persoz, 1833).

Payen and Persoz believed that in spite of all the information published about the composition and chemical reactions of starch, including the ones published by the manufacturers of alcoholic beverages, nothing had been reported about the economic extraction of the substance that destroyed the tegument of the grain and changed the starch into sugar and gum by means of water, heat, and germinated barley. The first objective was the isolation of the principle that converted dextrin into sugar. It was found to be a white amorphous solid, insoluble in alcohol, soluble in water and diluted alcohol. The aqueous solution was neutral and almost tasteless and was not precipitated by lead sub-acetate; abandoned to itself it promptly decomposed at room temperature and became acid. Heated with starch at 65^0 to 75^0C it possessed the remarkable property of breaking instantly the envelopes and liberating the dextrin, easily soluble in water, while the insoluble teguments floated or precipitated, according to the density of the liquor. This easy separation led Payen and Persoz to name the principle *diastase* (from the Greek: separation) (Payen and Persoz, 1833).

Payen and Persoz wrote that proper management of this process produced a very pure dextrin, with a rotation power higher than the product obtained by any other process. Diastase was also present in the germinated seeds of barley, oat, and wheat. Sometimes it was always accompanied by an azotized substance, which was soluble in water, insoluble in alcohol, capable of being coagulated by heat, incapable of acting on starch, and being precipitated from its solution by lead sub-acetate.

Payen and Persoz described the process for obtaining diastase from germinated barley as follows: One part of freshly germinated barley was powdered, mixed with half a part of distilled water and then macerated for a few minutes and filtered. The filtrate was heated in a water bath to 70^0C to coagulate the azotized substance and the mixture filtered again. Addition of alcohol precipitated the diastase leaving the sugar in solution. Purified diastase was obtained by repeated precipitation with alcohol. Payen and Persoz also gave a detailed description of their process for preparing dextrin in large quantities (Payen and Persoz, 1833).

Payen and Persoz summarized their results as follows: (1) raw dextrin was composed of three teguments, one insoluble in cold water and soluble in hot water, colorable by iodine and identical with the internal matter of starch; another soluble in cold and hot water and diluted alcohol, not colorable by iodine, similar to a gum; and third, a sugar soluble in water and alcohol of 35^0, not colorable by iodine and fermentable; (2) the prolonged action of diastase reduced the three teguments into two others which carried the transformation of the first tegument; (3) the teguments, isolated of the substance that enveloped them, were not colored by iodine as was whole starch; (4) the iodine coloring and discoloration phenomena occurred at different temperatures and depended on the relative solubility of the blue compound; and (5) the three substances, separated or together, had a large number of industrial applications and could also be used to study vegetable physiology (Payen and Persoz, 1833).

Amidone

In a following paper Payen and Persoz reported the results of their work about *amidone*, the internal substance of starch, and also provided additional information about diastase: (1) the starch of grains, potatoes, etc. were formed of amidone and teguments; (2) the teguments varied in different starches by the presence and proportion of an acrid, disagreeable, and tenacious substance, which gave them their special taste. This substance was insoluble in water and soluble in alcohol; (3) the reaction of water, a solution of iodine, baryta water, limewater, and diastase, occurred s the teguments. Diastase caused the rupture of the tegument by an osmotic effect, which determined the formation of two soluble substance; (4) amidone was chemical identical in all starches but varied in volume and cohesion; (5) amidone was insoluble in cold water but allowed it to penetrate between its particles and swelled them by degrees; (6) amidone had a spongy texture structure; when stretched by a short boiling in 100 times its weight of water it did not seem to have really dissolved, in spite it mostly passed through a filter; (7) the above properties explained de formation and properties of the jelly with different starches; (8) the teguments, entirely deprived of amidone, did not become blue with iodine; (9) amidone, alone in the starch, produced alternately the phenomena of coloration and discoloration, of opacity and diaphaneity, produced by iodine, alcohol, and water; (10) the diastase, water, and temperature transformed amidone only into sugar and gum. The sum of the weights of sugar and gum produced was equal to the weight of the amidone; (11) the action of diastase was not affected by presence of many substances, soluble or insoluble, neutral or slightly acid or alkaline, but could be hindered by tannin. The latter formed a compound with amidone, insoluble in cold water and increasingly soluble in water above 35^{0}C; (13) raw solutions containing diastase could be deprived of certain coagulable organic or coloring substances by heating to 75^{0}C, or by filtration over active carbon; (14) during the first development stage of certain plants the diastase was located precisely at the point where the starch ought to be rendered assimilable; the tegument was hereafter eliminated and the insoluble starch transformed into two soluble substances capable of being absorbed by the plant; (15) diastase was only capable of transforming amidone and had no action upon the gum, inulin, albumen, gluten, teguments, and lignin; (16) the starch was composed of about 99.5% of starch, while the teguments, deprived of all amidone, made up most of the remainder; (17) amidone was precipitated by alcohol, tannin, lead sub-acetate, baryta water, and limewater; and (18) diastase had become an important agent in the chemical analysis of starch and formed an easy means of making commercial dextrin (Payen and Persoz, 1834).

Osmium and Iridium

In 1833 Persoz described an improved method for preparing iridium and osmium, two metals Smithson Tennant (1761-1815) had isolated in 1804 by from the residues of the platinum mineral (Tennant, 1804; Persoz, 1833). Persoz's method was based .the reaction of crude platina with mixtures of sodium or potassium carbonate with sulfur, which produced the sulfides of iron, osmium, and iridium, and a silicate of these bases, and which collected in the form of scoria on the surface of the fused mass. The action of oxygen at a high temperature on the osmium sulfide resulted a blue volatile compound, described by Jöns Jacob Berzelius (1779-1848) (Berzelius, 1803).

Basically the procedure consisted in mixing one part of ore (after treatment with aqua regia), with two of sodium carbonate and three of sulfur and then dropping the mixture into a strongly heated earthen crucible. The crucible was then covered, heated to whiteness for a few minutes, and then allowed to cool. According to Persoz, the resulting contents consisted of three layers. The lowest one contained nearly all the sulfides of the platinum metals and was covered by another layer composed by pure sodium sulfide encompassing in its center a small quantity of osmium sulfide crystals. The surface of the fused mass was the crust of silicate of a light brown color. The scoria was separated as well as possible and the remaining two layers were treated with water to dissolve the remaining alkaline sulfides, the platinum disulfide, and the sodium sulfide attached to the sulfides of osmium and iridium. The residual mass was treated with a hot aqueous diluted solution of HCl to decompose the iron sulfide into ferric chloride and hydrogen sulfide. The liquid was separated by filtration and the new residue heated with three times its weight of mercuric sulfate to leave a solid composed of iridium oxide and expel the osmium oxide and metallic mercury. Pure iridium was obtained by heating the oxide in a porcelain tube and reduction with a current of hot hydrogen. The osmium was easily separated from the mercury by slightly heating the mixture in a somewhat inclined glass tube, while passing a current of hydrogen. The mercury was volatilized leaving a residue of pure osmium (Persoz, 1833).

Persoz ended this memoir indicating the remarkable action exerted by potassium bisulfate and an alkaline chloride on metals in general, and on those of the platinum group in particular: chloro salts were produced capable of decomposing sulfuric acid into sulfur dioxide and oxygen. The latter reacted with the alkaline chloride liberating chlorine, which reacted with the metal forming an acid chloride, able of combining with the non-decomposed alkaline chloride to generate double salts (Persoz, 1833).

Double pyrophosphates

In 1834 Persoz proposed a new method for separating metallic oxides based on the property of pyrophosphoric acid of forming with ammonia and the oxides, salts having different solubility. The pyrophosphoric was prepared by calcination of pure ammonium phosphate. The corresponding memoir included a description of the separation of the oxides of cobalt and nickel, cadmium and bismuth, lead and mercury, and uranium, cobalt, nickel, and zinc (Persoz, 1834b).

For example, to separate cobalt oxide from nickel oxide it was necessary to dissolve their mixture in nitric or hydrochloric acid, followed by addition of enough pyrophosphoric acid to saturate (neutralize) the two oxides. Addition of ammonia produced a precipitate, which disappeared on further addition of the base. The resulting solution was colored gray blue or violet, depending on the proportion of the oxides; left alone, the excess of ammonia evaporated and the solution became turbid. The deposit formed consisted of the double pyrophosphate of nickel and ammonia, colored initially gray and afterwards green. If the filtered solution did not contain nickel, it could be evaporated to a syrupy consistency without becoming turbid. The pyrophosphoric acid was separated from the nickel be means of hydrogen sulfide or sodium carbonate (Persoz, 1834b).

A similar procedure allowed separating cadmium oxide from bismuth oxide. In this situation bismuth pyrophosphate was insoluble in aqueous ammonia, while cadmium pyrophosphate was very soluble, as long as an excess of ammonia was present. Mixtures of the pyrophosphates of lead and mercury presented the same difference in solubility in aqueous ammonia: the former was insoluble and the latter was completely soluble. Uranium oxide was easily separated from the oxides of cobalt, nickel, and zinc by means of an excess of lead sub-acetate, which completely dissolved the oxides of cobalt, nickel and zinc (Persoz, 1834b).

Persoz continued his research on the subject by accident. As told by him, during a visit to the laboratory of Dr. Mathieu Joseph Bonaventure Orfila (1787-1853) a young chemist by the name of Roseleur showed him his application of a patent for a process for gilding in which pyrophosphoric was used as a solvent for gold. Persoz was very impressed by the idea but no so by the chemical explanation of the same. For this reason he decided to make a more detailed study of the chemistry and properties of pyrophosphoric acid and its double salts (Persoz, 1847a).

According to Persoz, present knowledge about the molecular composition of compounds had led several chemists to envision pyrophosphoric acid as capable of assuming several isomeric states in which its P_2O_5 molecule combined with the radicals RO, 2RO, and 3RO to give place to three different acids: (1) metaphosphoric (monobasic) phosphoric acid, (2) pyrophosphoric (dibasic) phosphoric acid, and (3) ordinary phosphoric (tribasic) acid. Although it was believed that of these three acids, common phosphoric was the one with the most tendencies to form double salts, Persoz proved that the tendency of pyrophosphoric acid was even larger. Alkaline cyanides, carbonates, and sulfides had a strong tendency to form double salts and dissolve gold in a state proper for gilding. Thus, it seemed natural to assume the formation of a double salt in the process proposed by Roseleur (Persoz, 1847a).

Except for very few exceptions it was known that addition of sodium or potassium phosphate to a saline solution produced a precipitate insoluble in an excess of the precipitant. This was the standard procedure for preparing phosphates but not the situation when the precipitant was an alkali pyrophosphate; now the precipitate formed was easily dissolved in an excess of the precipitant. The pyrophosphates of a strong base (such as those of calcium, barium, and silver), redissolved with the least facility in an excess of alkaline pyrophosphate. Pyrophosphates hardly precipitated a saline solution of weak bases (e.g. tin, gold, etc.). To explain these phenomena it was necessary to view the salts as bodies playing the part of bases and acids towards each other and capable of entering into combinations of a higher order (double salts). To accept this hypothesis required proving that alkaline pyrophosphates combined with other pyrophosphates, forming salts in which the insoluble pyrophosphate functioned as the electro-negative element, and the alkaline pyrophosphate as the positive one. This assumption could be proven by known experimental results: the substantial change, and sometimes complete disappearance, of the physical and chemical properties of the elements, which had entered into the combinations. For example, the characteristic taste and color of iron salts were completely absent in the double compound of pyrophosphate of iron(III) and sodium. Ferric salts were known to precipitate with hydrogen sulfide; no precipitate was formed when this acid was added to a solution of the double pyrophosphate of iron(III) and sodium. The definite proof of the existence of the double pyrophosphates was the actual production of some double pyrophosphates in a crystalline form of constant composition (Persoz, 1847a).

Persoz prepared these salts by two methods: (1) Addition of a solution of alkaline pyrophosphate to a the solution of the other salt until no further precipitate was produced; the insoluble pyrophosphate was then filtered, washed, and digested with a solution of pyrophosphate of sodium or potassium, which acted the part of a base, and the solution was then left to evaporate, and (2) diluting sufficiently a solution of the chloride or sulfate of the metallic oxide, which was to yield the insoluble pyrophosphate, to avoid the formation of a dense a precipitate; followed by addition of the alkaline pyrophosphate, in the stoichiometric necessary for the solution of the precipitate. Under these conditions the solution would contain the double pyrophosphate, the excess of alkaline pyrophosphate, and the chloride or sulfate of potassium or sodium (Persoz, 1847a).

Persoz detailed the preparation and properties of many double pyrophosphates, among them, magnesium and sodium, uranium and sodium, chromium and potassium, aluminum and sodium, iron(III) and sodium, iron(II) and sodium, copper and sodium, copper and potassium, and gold and sodium (Persoz, 1847a).

Atomic mass of carbon

In 1840 Jean-Baptiste André Dumas (1800-1884) and Jean Servais Stas (1813-1891) reported that the results of their experiments indicated that there was a serious error, of about 2%, in the value of atomic mass of carbon suggested by Jöns Jacob Berzelius (1779-1848) for this element. According to Dumas and Stas oxygen and carbon united to form CO_2 in the ratio 800 to 300 and not 800 to 306, as claimed by Berzelius. This error indicated the need to correct all the values of atomic masses of the elements reported thus far. If their claim was true, then there was also a need to change accordingly, all the reported chemical formulas reported in the literature (Dumas and Stas, 1840).

In their experiments Dumas and Stas burned a known weight of pure carbon with oxygen and weighted the amount of CO_2 formed. The carbon they used originated from three sources: (1) natural graphite taken from the chemical collection of the Jardin du Roi, (2) artificial graphite extracted from the iron mass produced in a blast furnace, and (3) a diamond. All these samples were carefully treated to eliminate foreign impurities (earth, iron, sand, etc.); for example, they were heated red in the presence of KOH, boiled in nitric acid, treated with dry chlorine and aqua regia, etc. The purified graphite was dried by heating at a high temperature, followed by cooling in the presence of sulfuric acid. The purified and dry graphite was put in a small glass boat located in the middle of a meter-long glass tube and burned with oxygen originating from a hot mixture of cupric oxide and potassium chlorate and purified and dried by passing through limewater, a solution of KOH, and sulfuric acid. The memoir gave a detailed description of all the measures taken to assure the purity of the oxygen and the full oxidation of the carbon sample.

The results of the experiments indicated that 800 part of oxygen combined with 300 of carbon to yield 1100 of CO_2, that is, a ratio of 8 parts of oxygen for 3 of carbon (Dumas and Stas, 1840).

A year later Persoz published the results of some experiments that suggested the need of decreasing the accepted value of the atomic mass of carbon (75) (Persoz, 1841a). He had burned 2.5 g of sugar with mercury sulfate of mercury and obtained 3.919 L of gases (measured at 0^0C and 760 mmHg) instead of the 3.868 L or 3.912 L required using the atomic mass of carbon suggested by Berzelius and Dumas, respectively, and Liebig's atomic formula of sugar (Liebig, 1839).

According to Persoz, the only thing which remained to be decided, and which was equally important, was the accurate determination of the equivalent of carbon. Should the number 75, admitted by Dumas and Stas, be adopted, or should another be sought? His results clearly indicated that all the combustions he had carried on in the presence of mercuric sulfate generated more CO_2 that the amount calculated assuming an atomic mass of 75. Persoz attributed the discrepancy between his results and those of Dumas and Stas to the mode of collecting the water in the combustion of carbon and organic matters. The results of his experiments carried on at 11^0C, and 757 mmHg indicated that one volume of concentrated sulfuric acid absorbed exactly one volume of CO_2, suggesting that the employment of sulfuric acid for determining water in organic analyses could lead only to false results (Persoz, 1841a).

This memory contained Dumas criticism of Persoz's experimental procedure and calculation methods. Dumas wrote that in burning sugar and measuring the volume of the resulting gas, Persoz had necessarily assumed his sugar was pure and that he had reduced the weight in *vacuo*; that the expansion coefficient of gases was accurately known and the gases followed Dalton-Mariotte's law, that his gases were absolutely dry, that the density of carbonic and sulfurous acid gases was perfectly know (which was not true, at least, so far as regards CO_2). Although Persoz had used a completely different experimental method, his result differed only 1/800 from that which Dumas and Stas had obtained in experiments free from any data, by simply weighing the carbon burned and the CO_2 obtained. Dumas believed that Persoz was wrong in assuming that the difference was caused by the absorption of CO_2 in sulfuric acid. He wrote "the learned chemist will without difficulty be convinced, if he will be kind enough to repeat our experiments, or at least some of our analyses" (Persoz, 1841a).

Oxidation of gelatin

According to Persoz, gelatin was a neutral, nitrogenous substance, which under an oxidizing influence, converted mainly into hydrogen cyanide, ammonia, and CO_2, accompanied by a small quantity of one of the volatile, odorous, fatty acids discovered by Michel Eugène Chevreul (1786-1889) (Persoz, 1841b). He gave the following example of such oxidation: 40 g of gelatin dissolved in two liters of warm water, acidulated by 300 g of sulfuric acid, were introduced into a tubulated 3-liter retort connected to a receiver fitted with a tube for collecting the gases. The cooled solution was mixed with 160 g of potassium dichromate and then heated. A reaction promptly begun accompanied by the release of a large amount of gas, while a small amount of oily matter deposited on the surface of the liquid, and a almond smelling liquid almonds in the receiver. Chemical analysis indicated the gas was CO_2 pure, the condensate contained HCN, and the residue of the distillation contained chrome alum derived from the reaction of the dichromate with the elements of the gelatin, and ammonium sulfate (Persoz, 1841b).

Persoz remarked that his experiments did not throw light of the molecular arrangement of the elementary principles of gelatin. However, he believed that the products resulting from the oxidation of gelatin by potassium dichromate should be similar to those generated by the same organic matters, when, under suitable circumstances, they were transformed by the air or by oxygen. Nevertheless he speculated if chemical analysis would show whether among the products of the normal or abnormal secretions of the skin, some ammonia, hydrocyanic acid and its compounds were not formed, namely, the compounds of cyanogen and formic acid. As a possible proof of this assumption he reported that his friend Dr. Auguste Nonat (1804-1887), then a student at the hospital at the Hôtel Dieu, had brought him some lint and bandages stained of a bluish green by their contact with the purulent matter of the wound of a patient. Was it possible that this color could be attributed to the Prussian blue which may have been formed by the action of the pus on the iron rust, which may accidentally have existed on the linen and lint used for dressing the wound (Persoz, 1841b).

Iodine recovery

In 1847 Persoz wrote that the increasing use of iodine in medicine had led to a continuous rise in its price, and that this circumstance had led him to investigate the possibility of recovering the element from the aqueous solutions in which it existed naturally, from medical prescriptions, and even from the urine of sick people being treated with iodine (Persoz, 1847b). Eugène Souberain (1797-1859) had found that the industrial method for extracting iodine from the mother liquor of varech soda was too tedious and expensive, and had proposed an alternative procedure in which the first step was the separation of the iodides from the accompanying chlorides and nitrates. This objective was easily achieved precipitating the element with cupric sulfate mixed with iron fillings, decomposing the resulting cuprous iodide with sulfuric acid or manganese dioxide, followed by distillation or sublimation of the iodine. Later on the process was modified by replacing the iron filings with ferrous sulfate (Soubeiran, 1827). Some years later, the substantial use of iodized baths at the Hôpital Saint-Louis tempted Labiche and Chantrel to carry on experiments for the purpose of economically extracting the element from the solutions. Their final procedure was based on precipitating the iodine with starch, followed by decomposition of the precipitate with chlorine, addition of more starch mixed with a large amount of water, separation of the new precipitate, followed by treatment with a current of SO_2. The resulting SO_3 and hydrogen iodide were neutralized with KOH and the resulting solution evaporated to a syrupy consistency. The iodine was then separated using sulfuric acid or manganese dioxide. Labiche and Chantrel also found that the iodine contained in the complex with starch could be easily separated by incineration with an alkali (Labiche and Chantrel, 1846).

According to Persoz, Labiche and Chantrel had overlooked the important fact that iodine combined with starch only when it was in a free state; it was consequently necessary to liberate it from its combinations by means of chlorine, an extremely difficult operation. To avoid this problem Persoz tried several other reagents (such as ferrous acetate, SO_2, etc.) and found that SO_2, a well-known powerful reducing agent, was the most appropriate. Eventually he developed the following process: First, the amount of iodine was determined in the solution to be treated, second, one part of cupric sulfate and three of sodium bisulfite were added, calculated upon the fact that about 3 parts of the cupric sulfate were required for one part of potassium or sodium iodide. The liquid was then left alone or boiled, according to whether the precipitate was desired immediately or after a few hours. The precipitate was filtered, washed, dried, and the iodine extracted by one of the known processes, including calcination. Persoz believed that his procedure was so simple and fast that in future all iodized waters would be treated as indicated. He also believed that his method could also be employed for the analysis of mineral waters containing bromine and iodine (Persoz, 1847b).

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