François Antoine Henri Descroizilles

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RESUMEN. François Antoine Henri Descroizilles (1751-1825), un farmacéutico Francés, dedicó la mayor parte de su vida a actividades industriales y al desarrollo de instrumentos y métodos para analizar productos químicos de interés general, entre ellos, un destilador portátil para la industria vinera, un aerómetro, un clorómetro para determinar la concentración del cloro en solución acuosa, y un alcalímetro para determinar la concentración de NaOH o KOH, como tales o como sus sales, Se le puede considerar como el fundador del análisis químico por volumetría.

ABSTRACT. François Antoine Henri Descroizilles (1751-1825), a French pharmacist, spent most of his life in industrial activities and the development of instruments and apparatuses for analyzing chemical products common interest, among them a portable alembic for the wine industry, an aerometer, chlorometer for determining the concentration of chlorine in its solutions, and an alkalimeter for determination the concentration of NaOH and KOH, as such or in the form of salts. He may well be considered the founder of volumetric analysis.

LIFE AND CAREER[1-4]

François Antoine Henri Descroizilles was born on 11th June, 1751 in Dieppe, the son of Marie-Reyne Biel and François Descroizilles (1707-1783), a pharmacist who had studied under *Étienne François Geoffroy* (1672-1731) in Paris, who also served as judge of instruction of the city merchants, and was corresponding member of the *Académie des Sciences*, *Arts et Belles-Lettres of Rouen*. There were sixteen brothers and sisters, of which nine died at a very early age. Henri Descroizilles studied at the Oratorian College in Dieppe, and under the direction of his father he became very interested botany and marine flora. After graduation his father sent him to Paris to study and work in the laboratories of Hilaire-Marin Rouelle (1718-1779) (Rouelle the Young) and Louis-Jacques Thenard (1777-1857). In 1777 he finished his studies and returned to Rouen carrying a certificate of *démonstrateur royal de chimie*, and permission for apprenticeship, issued in Versailles the same year. The latter was a compulsory requirement for establishing a pharmaceutical business in a large city, after passing the required examinations and the rituals of the profession. In his PhD thesis, Louis Constant Victor Simon gives a very detailed description of all the requisites and demands to be fulfilled by a candidate to the apothecary profession, including a hefty fee for the benefit of the poor in the General Hospital, payment of an honorary to the members of the jury, and participation in the banquet that signaled the end of the examinations.[3]

After passing all the exams and receiving his license of Maître de l'État d'Apothicaire, Épicier et Cirier (pharmacist, druggist, and chandler), Descroizilles bought the pharmacy of Le Danoys and began a successful business career, while simultaneously carrying on research on a wide variety of practical subjects such as the invention of a flashing lighthouse (*phare de éclipse*) to guide ships coming into the port of Dieppe, and a coffee maker (*cafetiére*), which may be considered the father of the present coffee pot.[1]

While in Rouen, Descroizilles became a close friend of Jean-Marie Roland de la Platière (1734-1793) and his wife Marie-Jeanne Phlipon (Madame Roland) (1754-1793). Roland was a leader of the Girondist faction during the French Revolution, and future Minister of Internal Affairs (In this position Roland appointed Descroizilles Inspector of markets in the Dieppe area). Eventually the Girondists came into attack, forcing Roland into hiding. He was condemned to death in absentia; his wife remained in Paris and was arrested and executed. Descroizilles was accused of royalism and federalism, and was incarcerated in the house of Saint-Yon, the political prison of Rouen. During this period he found a better method for rapidly purifying of saltpeter (KNO_3) scrapped from caves and old buildings. A close friend took care of communicating this information to the Comité de Salut Public. It seems that for this reason he was released from prison and appointed member and inspector of the Administration des Poudres et Saltpetre in the Department of Lower Seine and adjoining departments. In this new position he became well acquainted with Claude-Louis Berthollet (1748-1822) and Gaspard Monge (1746-1818), two important scientists members of the Administration.

His many industrial activities led to his election as resident member of the Académie des Sciences et Belles-Lettres de Rouen (1804), particularly because of his memoir about all the water fountains of Rouen and Dieppe[5], which became part of the book published by Louis Lepecq de la Clôture (1736-1804), *Sur les Maladies et Constitutions Épidemiques*[6]. In 1806 Descroizilles moved to Paris and was appointed member and secretary of the Conseil Général des Manufactures, a position he lost in 1815 for political reasons. In 1806 the jury of the Rouen Exposition awarded him a gold medal for having established in 1788 at Lescure-lès-Rouen, one of the most successful establishments for bleaching using Berthollet's procedure. In 1816 the Ministry of the Interior appointed him member of the panel jury to decide about fabrics of foreign origin, for the protection of the national industry. In 1819 Descroizilles published a booklet describing a very simple method for the preservation of cereals based on drying the grains completely by heating before being packed in sacs[7], and another for marking goods, in such a way as to identify their origin and the nature fabrics employed in their fabrication[8].

Some of his significant achievements are the development of analytical procedures for detecting the presence of foreign substances in cider[9]; the etching of glass means of HF[10]; a comparison of Roman and synthetic alums[11]; the design of an aerometer, which allowed the determination of the specific gravity of a liquid, relative to the specific gravity of a given substance[12]; development of an industrial procedure for manufacturing industrial quantities of cupric sulfate, zinc sulfate, and tin nitrate (an important constituent of mordants), to replace the imported salts[13]; the use of fumigation and sterilization using chlorine and its aqueous solutions[14]; and the design of a portable alembic for determining the alcohol content of wines[15]. His most important contributions were the development of a volumetric method for determining the amount of chlorine present in bleaching waters and the amount of alkali present in commercial KOH and NaOH, and their salts[10,16,17].

Descroizilles passed away on April 15, 1825 and was buried in a temporary tomb in the Père Lachaise cemetery; after the prescribed period his rests were transferred to an unknown common tomb.

Scientific contribution

Descroizilles wrote about 15 papers, most of them on practical aspects of chemistry. Some of them were published as booklets (e.g.[7,8,10,15,16]). Here we describe is most important results.

Cider adulteration

In 1786 the Parliament of Rouen requested from the King to appoint a committee composed of members of the Académie des Sciences, of the Faculté de Médicine, and the Collège de Pharmacie of Paris, to carry on experiments on all the stages of the manufacture of ciders and pear liquor, to determine to determine the effects, positive or negative, of substances added to these drinks, in order to sweeten their taste. They also requested to issue the necessary regulations to insure the safety of the public and the benefits of commerce. As a result of this letter the Académie appointed a committee composed of Antoine Alexis-François Cadet de Vaux (1743-1828), Antoine Baumé (1728-1804), Claude-Louis Berthollet (1748-1822), and Antoine-Laurent Lavoisier (1743-1794), and the Société Royale de Médicine appointed another one composed of Michel-Augustin Thouret, Lavoisier, and Antoine-François Fourcroy (1750-1809). Each committee issued it's own report.[9,18] The report of the Académie mentioned the work of Descrozilles and so it will be described here.

The first part of the report described the events that had taken place in Normandy related to the falsification of ciders. Historically, the cider industry had developed several processes for sweetening cider that had become sour, to clarify the juice, and to stimulate its fermentation, little favored by the cold season during which the process was carried on. Some of the materials added for these purposes were dangerous to health and could be considered as true poisons. In 1775, after serious health incidents caused by white lead (used for clarification purposes), an edict was issued prohibiting the use of this and other lead compounds, in any of the processing stages of cider production. The edict contained a procedure for detecting this compounds by means of ammonium sulfide. In the same year, a chemist from Rouen, named de la Follie, published a paper indicating that the sulfide test was insufficient because adding chalk to the cider could mask the presence of lead. Not only that, the chalk added was also deleterious to health. De la Follie stated that the presence of chalk in cider could be detected by addition of a fixed alkali (KOH or NaOH).[19]

De la Follie findings led to the issue of new edicts prohibiting the addition to cider *of any ingredient or foreign body*, and establishing corporal or pecuniary sanctions to anyone found violating the ordinance. The police was ordered to visit routinely the caves and cellars were the cider was prepared and kept, and take samples to be analyzed by Pierre François Mésaize (1748-1811), Rouen's chief health pharmacist and head pharmacist of the Hospital Dieu of Rouen. These draconian regulations were based on the assumption that formation of a precipitate by the action of alkali meant that the cider had been adulterated by addition of a calcareous substance, and that the presence of such a substance masked the presence of lead compounds.

In 1777, Descroizilles, then a pharmacy student, published a note in the *Affiches de Normandie*, claiming that the precipitation caused by an alkali did not mean necessarily that a calcium compound had been added to the cider; this substance could well have originated from the hard waters used in the preparation of the cider. Descroizilles's publication led to a bitter polemic, which resulted in Descroizilles being brought to trial and condemned for damaging the reputation of the police lieutenant general of Rouen. The Rouen Parliament eventually rejected the sentence and also ordered that additional experiments be conducted to test the validity of the analytical procedures in use.

Lavoisier's committee decided to work on their own cider in order to decide the question of the origin of calcium compounds in the cider. For this purpose they brought to Paris a large amount of apples and installed a small-scale plant to produce the cider from crushed fruits, under the following various conditions: (1) crushed in a wooden mortar, put in a cave, open the atmosphere, and left to ferment without addition of water; (2) crushed in a wooden mortar, put in a cave, open the atmosphere, and left to ferment after addition of water from the Seine river; (3) crushed in a wooden mortar, stored in a cask and left to ferment without the addition of water; (4) crushed in a wooden mortar, put in a cave, open to the atmosphere, and left to ferment after addition of water from a well; (5) crushed in a wooden mortar, stored in a cask and left to ferment after addition of water from a well; and (6) crushed in a stone mortar, put in a cave, open to the atmosphere, and left to ferment without water. All the resulting ciders were found to be acid in different degrees, and except for the last one, or those prepared with well water, they produced no precipitate with alkali. The last result indicated that the acetic acid produced by the fermentation was able to attack the stone mortar and generate a stony salt. Mésaize carried the alkali test without information about the origin of the cider; he testified that according to the present regulations he would have declared ciders #4 and 5 to be unacceptable for commerce as such; they could be distilled to produce a fruit brandy.

These experiments led to the following conclusions: (a) the earthy precipitate obtained from some of the ciders upon addition of alkali did not prove that they contained added chalk; (b) the additions of cinders, limestone, or lime, did not prevent the precipitation of lead when treating the cider with ammonium sulfide; (c) the addition of cinders, alkali, chalk, and limestone, in a reasonable amount to sweeten the cider was less damaging to the health than the original acidity; (d) although the addition of white lead and other lead compounds should be severely punished by the tribunal, their presence should be proven by more delicate tests than using ammonium sulfide; (e) since copper or its derivatives were unable to repair the taste of sour juices, their presence could be attributed to purposely addition; the metal probably originates from the metallic vessels used to keep the cider; (f) the addition of lead compounds should be prohibited by law; and (g) the use of cinders, alkali, chalk, and other absorbants, as clarifying agents, should be regulated by law.

The experiments carried by the committee justified Descroizilles's claims that the precipitate produced by the addition of alkali did not prove that chalk had been added to the cider; it was possible that the chemical originated from the use of a stone mortar or from the hard waters using during the process. In addition, the addition of chalk did not mask the presence of lead.

The resulting conflict with Mésaize led Descroizilles to return his license to operate a pharmacy (the pertinent letter to the Maitres en Pharmacie of Rouen appears in the book by Simon.[2]

Glass etching with hydrogen fluoride

In 1778 de Puymaurin published a paper describing the action of HF on glass and its application to the etching of glass.[20] The paper was prefixed by an editorial note indicating that the priority of the discovery belonged to a German scientist by the name of Count de G***. G***'s process was based on covering the glass with melted wax or engravers varnish, drawing the lines with a graver, and treating the nude areas with a mixture of equal parts of sulfuric acid and fluorspar. To prevent evaporation, the glass plate was covered with a porcelain plate. After two or three days the process was complete and the porcelain plate and remaining wax removed, to expose the etching.

According to de Puymaurin, previous workers had already reported that a mixture of sulfuric acid and fluorspar corroded glass and that during distillation of the mixture, an acid gas was released, which was highly soluble in water and covered its surface with a crust. De Puymaurin believed that if the mixture was distilled in a metal retort, the acid obtained contained some of the metal retort and a quantity of siliceous earth, which were easily shown by their precipitation with a caustic alkali. These impurities were the ones forming the crust on top of the water. In addition, the distillation should always be carried on in a water bath because otherwise the sulfuric acid would rise into the receiver. The calcium sulfate formed would affect the drawing and produce an uneven etching. For these reasons, de Puymaurin suggested that the distillation be carried in a lead retort and the resulting acid be kept in vessels coated in the inside with a mixture of wax and oil. This gaseous HF applied to glass rendered its smooth surface rough and corroded it as rapidly as nitric acid corroded copper and other metals. De Puymaurin engraving procedure consisted in covering a glass plate with wax, and after having designed figures upon it, covering the plate with hydrogen fluoride and exposing it to the sun. After five hours the wax was removed from the glass, and the acid washed with water. De

Puymaurin believed that his procedure could be used to graduate scientific instruments, replacing the copper and wooden scales presently used, and to etch in glass bottles the names of reagents being stored.[20]

According to Descroizilles, de Puymaurin method was fast and efficient, but was only applicable to flat surfaces. He suggested that a better procedure for preparing the acid and carrying the etching process was to put a mixture of equal parts of sulfuric acid and powdered fluorspar in a vessel having its internal surface coated with wax. The surface to be etched was prepared as before and exposed to the vapors while hanging in the neck of the vessel from a wax stopper, for avoiding the gas to escape into the laboratory. The whole setup was maintained at about 25^0C for 12 hours to complete the etching process. Descroizilles also described the construction of an apparatus for etching various elements simultaneously.[21]

Titration of chlorine

Until the eighteenth century, the crude fabrics manufactured from vegetable fibers had a grey color and were bleached by lengthy primitive methods, involving repeated washes with stale urine, potash, sour buttermilk, or sulfuric acid, followed by exposure to sunlight for three to sixth months. The process was very lengthy and expensive, depended on the weather, utilized vast areas of land that could not be cultivated, and required vigilance against robbery.[22] This situation begun to change when in 1774 Carl Wilhelm Scheele (1742-1786) found that heating hydrogen chloride with manganese dioxide (pyrolusite) released a yellowish-green gas (*dephlogisticated marine acid gas*) that smelled like warm aqua regia, was soluble in water, and bleached paper colored with litmus; green vegetables, and red, blue, and yellow flowers nearly white. The color was not restored by treatment with acids or alkalis.[23] Two following papers by Claude-Louis Berthollet (1748-1822) gave a thorough description of the gas and its bleaching properties, as well as of a procedure for manufacturing it in large quantities. Chlorine was generated using Scheele's method; sulfuric acid was poured on an appropriate mixture of manganese dioxide and salt and the gas liberated collected in water.[24,25] Interesting enough, Berthollet, in his 1789 paper, mentioned that Descroizilles had found a cheaper procedure for manufacturing chlorine: "…Mais un habile chimiste de Rouen, M. Décroisille (sic), qui faisoit aussi des épreuves dans la vue de faire un établissement dans cette ville, publia dans les Affiches de Normandie, qu'il avoir trouvé un moyen de se procurer l'acide muriatique oxigèné à un prix fort inférieur à celui du procédé que j'avoirs indiqué…" (a skillful chemist from Rouen, M. Décroisille, who made attempts to start a plant in the town, published in the Archives de Normandy, that he had found a new method for preparing oxygenated muriatic acid by a lower price than that prepared by the process I have described).[24]

Many French and English industrialists tried to put into commercial practice Berthollet's procedure; most of them failed when it was found that direct treatment of the cloth with chlorine was inadequate; the gas was obnoxious and caused serious health damage to the workers; in addition it led to extensive cloth damage. Descroizilles joined forces with Alexandre de Fontenay, a manufacturer who served as mayor of Rouen, to install a bleaching factory in Lescure-lès-Rouen; this enterprise almost failed until Descroizilles realized that the secret for the correct bleaching of clothes was controlling the strength of the aqueous solution of chlorine. In 1791 he succeeding in developing an instrument, which he named berthollimètre, able to analyze these solutions and determine their concentration. The berthollimètre was based on the ability of chlorine, dissolved in water or combined with an alkali, of decolorizing indigo. The change in color was proportional to the concentration of chlorine. Descroizilles published his findings in the Archives de Normandie, in the Journal des Arts et Manufactures, and also in the form of a booklet.[10,26]

In the introduction to his paper, Descroizilles defined a series of new terms, based on the name of Berthollet. Thus, the aqueous solution of chlorine was called *lessive de Berthollet*, *blanchisserie berthollienne* was the bleaching procedure based on chlorine, *berthellorie* was an industry using the procedure, *bertholleurs*, were its workers, etc. etc. The berthollimeter was a graduated glass tube, 24 to 25 cm tall and 14 to 16 mm diameter; carrying 24 mayor marks, each subdivided in four subdivisions. The berthollimetric fluid was prepared by adding one part of finely divided indigo to eight of concentrated sulfuric acid and heating the mixture in a water bath until total dissolution. After cooling, the solution was diluted a thousand parts of water. A given amount of the indigo solution (the standard) was put into the marked glass tube and chlorine water added until total decolorization. The volume added was a measure of the relative concentration of the chlorine solution. In this manner it was possible to determine the relative concentration of the chlorine water, which had been found appropriate for cloth whitening. Descroizilles indicated that water saturated with chlorine at 10^0C gave a reading of 8 in his apparatus.[10]

Dangers of phosphorus

In 1801 Descroizilles described an accident that occurred him where a bottle, containing 100 g of phosphorus covered with enough water, burst by the freezing of the latter. As a result, some books, papers, and a cupboard caught fire and he was almost suffocated by the strong vapors of phosphorus pentoxide.[27] The fire was extinguished with the help of his assistant. According to Descroizilles, the bottle was wrapped in papers, which absorbed the water and allowed the phosphorus to become in contact with air. In a letter to the editor, he cautioned the readers to avoid keeping phosphorus in the above manner and recommended that the bottles should always be placed in copper cases lined with bran and paper.[27]

Fire extinction

In a letter written to Berthollet, Martinus van Marum (1750-1837) described the experiments he had carried on to show how it was possible to extinguish violent fires with a very small amount of water.[28] Van Marum had heard of a liquid called anti incendiary, developed in Sweden by van Aken, able to extinguish fires in very small amounts. This particular liquid was an aqueous solution containing 40 kg of ferric sulfate, 30 kg of aluminum sulfate, 20 kg of iron red oxide, and 200 kg of clay (van Marum did no report the amount water). Van Marum formed two identical combustible masses (barrels containing pitch), set them on fire, and extinguished one of them with van Aken's liquid and the other with common water. This experiment was repeated several times. To his surprise, van Marum found that the van Aken solution had no advantage over plain water, but that very violent fires could be extinguished with very small amounts of ordinary water. Van Marum explained this result on the basis of the well-known fact that the flame of a burning body extinguished when its contact with atmospheric air was prevented; in his experiments the steam generated achieved this goal. Hence it appeared that it was possible to extinguish a violent fire by adding a small amount of water to the zone were the fire was the most violent, followed by addition of water to the neighboring areas.[28]

On the basis of these results, van Marum recommended the Dutch citizens to provide themselves with small portable water pumps, for their use in case of need. He reported that his method was tested successfully in large-scale demonstration experiment carried in Haarlem (Holland) in May 1797, and in Gotha (Germany), the year afterwards.[28]

A year after, Descroizilles published a paper refuting the results of Van Marum. He reported that already in 1788 he had attended a fire extinguishing demonstration mounted by a person who claimed to have a secret formula for an anti incendiary liquid mixture. Again, the experiment was related to the extinction of the fire in a barrel containing pitch, located within a wooden structure. The final result was the total destruction of the wooden structure; extinction was possible only after using large amounts of ordinary water. As a result of his observations, Descroizilles concluded as follows: (a) A small amount of water was needed for extinguishing the flame of gums, resins, and fats and oils, spread over woody materials, where, initially, the latter provided a stage for the burning of the pitch, but when the wood itself began to burn, very large amounts of water were required for extinguishing the fire, using the standard method employed by the fire department of a large city; and (2) since the air passing through the heating pipes was loaded with humidity, it increased the burning phenomenon *because the water was decomposed; the oxygen attacked the metal, and the hydrogen ignited*.[29]

Descroizilles paper led to a polemic with Van Marum, claiming that extinguishing the fire originated by the pitch protecting the wood, was enough to avoiding ignition of the latter.[30]

The reader interested in the development of fire extinguishing methods is directed to a review paper published by Jean Baptiste Alphonse Chevallier (1793-1879) in 1851.[31]

Pickled violets

At the time of Descroizilles, syrup of violets was a standard reagent for recognizing the presence of uncombined acids or alkalis, or of alkaline bicarbonates (it turned red in the presence of acids and red in the presence of alkalis), although it could not be kept for long time without decomposition. In order to overcome this problem, Descroizilles modified the usual method of preparation of the syrup by adding common salt, and obtaining an infusion which he called *pickle of violets*.[32] In his procedure the petals of violet were slightly pressed into a small pewter, and then mixed with twice their weight of boiling water and stirred together. The resulting infusion was heated for a few hours at a temperature somewhat higher than that of boiling water, and then strongly pressed out through a very clean linen cloth. The filtrate was mixed with one-third its weight of common salt, very fine and white, to avoid the presence of calcium nitrate, which affected the color of the reagent (dark blue violet). According to Descroizilles, the resulting saline solution would keep in a corked phial without alteration, at various temperatures, even in the presence of direct sunlight. The pickled decoction was a better reagent than the best syrup of violets. Additional experiments proved that several other blue flowers, such as those of iris, larkspur, etc., also afforded a highly sensible pickle. To use this liquor as a reagent, a little stick was dipped in the phial and the wet end made to touch a clean earthen plate in various places (easily up to 30 spots), so that, a few decagrams of the pickle were enough for making a large number of analyses in one year.

In the second part of his paper Descroizilles discussed the advantage of using common salt for preserving vegetables used for medical uses or perfumery, which had to be transported a long distance. He remarked that his teacher (Hilaire Marin Rouelle) used to perfume his laboratory for the period of the course of chemical lectures given in the winter of 1775 by distilling roses he had salted in the month of June. His rose water, mixed with sugar and alcohol, formed a delicious cordial. Descroizilles himself had kept a jar full of salted rose leaves in his laboratory for a period of three years, without their perfume losing nothing of its strength or sweetness. He explained that roses could be salted in the following manner: One-and a half a kilo and half of rose leaves, were bruised for two or three minutes with one third their weight of common salt. The flowers thus bruised gave out their juice and produced a kind of paste of little bulk. This paste was put in an earthen vessel and the process repeated enough times until the vessel was full. The vessel was closed and kept it in a cool place until needed. At this time the paste was distilled then and diluted with about double its weight of pure water. According to Descroizilles, this allowed distilling in Paris herbs salted long before in places the most remote from the capital. Some believed that waters distilled were more fragrant, and at the same time yielded more essential oil. In addition, it was possible to use the water while in full possession of its medical virtues.[32]

Some years later, Chevallier reported that in 1826 he had been requested to prepare water distilled from a large amount of orange flowers collected in a plantation near Orléans.[33] In spite of all the precautions taken to shorten the shipping time, it was found that on arrival de flowers had a dark yellow hue and an odor no so agreeable as the fresh ones. The oil prepared by distillation, instead of being transparent, had a red color similar to that acquired by bitter oranges prepared after a long time. In order to obviate these defects he decided to test the goodness of the procedure recommended by Descroizilles. He took two given (equal) weights of fresh flowers, mixed one portion with 20% its weight of common salt and the other with 25% weight salt, and stored the resulting homogeneous pastes in a closed barrel kept in a fresh place. After two years he opened the vessels, mixed each paste with twice its weight of water, and distilled the mixture in a common still. To his satisfaction he found that both pastes produced a very limpid distillate, having a soft taste. In other words, Descroizilles's procedure allowed preserving the roses for a long time, without decomposition, and produce a distillate as good as the one prepared from fresh flowers. Not only that, it was possible to reduce the amount of added salt from 25% to 20%.[33]

Water distilled from plants

According to Descroizilles, the fact that every plant had a smell peculiar to it, had led to classify them into odorous and inodorous plants. It was assumed that medicines obtained from odorous plants were more active than those from the inodorous ones, and consequently, the water distilled from the latter had no particular virtues and did not differ from distilled water. Descroizilles believed that this conclusion was ill founded and that the way to test it was by concentrating by distillation, as much as possible, the feeble aroma of the inodorous plants.[34] Since the first distillate contained very little odorous principle, his idea was to mix it with a fresh batch of the plant, collect the next first passing liquid, and repeat the process as many times as necessary (usually tree to four times) until the water became saturated with aroma.

Together with his assistant Clairon, he applied this procedure to twenty-five plants considered inodorous, until they felt that that the product had no increase in odorous quality. Their results indicated that all the final waters were transparent, had a peculiar very pungent smell, similar to those prepared from horseradish root or from scurvy grass, and generally, did not keep well. After some time they begun to lose their transparency, and acquired a very disagreeable smell, particularly when kept in transparent bottles ad exposed to sunlight. Anyhow, these waters were shown not only to have a clear medical advantage, but also a use in the arts. Descroizilles gave as examples the use of concentrate lettuce was as a substitute of laudanum, and that of *Argenteum alatum* (silverweed), for improving the look of silk gauze.[34]

Alkalimetry

In 1806 Descroizilles published his first memoir about commercial alkalis, reporting the result of his studies of the salts of potassium and sodium, their origin, and a new procedure to dosage the amount of alkali present in every salt. He studied in particular, three classes of potassium salts: those obtained from vegetables (Russia, Hungary, Trieste, and Danzig), pearl ashes, and very white potashes originating from America. Several of these potashes were of high quality and always contained potassium sulfate; others, such the American ones, were the product of the evaporation of a lye of cinders, chalk, and sodium chloride, others, very impure potashes.[16] Sodas had a different origin; the richest ones originated from Alicante, Languedoc, and Cartagena, and were obtained by drying and calcining several seacoast plants (halophytes) belonging to the genres *salsola* and *salicornia*. The bleaching plants paid for the different raw materials according to their alkali content. The complexity of raw materials had lead to the development of a series of analytical procedures, which not always agreed in their results. This situation led Descroizilles to develop a new apparatus (alkalimeter), which could be used universally as a standard for determining the alkali content of any raw material. His alkalimeter consisted to a glass tube, 20 to 25 cm long and 14 to 16 mmm diameter, sealed at one end and inserted into a pedestal, which kept it in a vertical position (in modern terms, this would be a burette). The upper end was partially closed with white wax, to prevent the liquids to flow along the external surface, to allow an easy filling and discharge, and to allow the air to escape. On this tube he engraved a scale of 72 equal parts (degrees) beginning from the top; so that each degree contained 0.5 g of the testing liquor. The latter was prepared by mixing one part of sulfuric acid of 66^0 Baumé (specific gravity 1.848) with nine parts of distilled water. To carry out the determination required a small balance and weights, a 50 cm^3 vessel, common table glasses, wooden stirring rods or matches (without sulfur), a mortar (for crushing hard raw materials), a tumbler glass and a plate, a solution of extract of violets, and litmus paper turned red by the testing liquid. The operating procedure was very simple. Ten grams of the potash to be tested were placed into a glass and dissolved in about 40 mL of water. The resulting solution was filtered through paper, and poured into a common tumbler. Then a few drops of violet syrup were distributed along the edge of the plate with the help of a wooden rod. The testing liquid was now poured into the glass tube up to the mark zero, and from there slowly transferred into the solution contained in the tumbler, while testing the latter all the time with violet syrup to determine when it became neutralized. This operation had to be repeated frequently as the titration continued, until the color of the violet drop turned from green to red when the saturation (neutralization) point was reached. The average value of potash was 55 degrees, which meant that 55 parts of sulfuric acid were required for neutralization, if it consumed less than this volume then it was not of sufficient quality. Obviously, Descroizilles did not calculate the absolute value of the strength of the potash; he was satisfied with a relative result, which was quite sufficient for practical purposes in the factory. The only information required for control purposes was whether a 10 g sample of the potash required 55 volumes of sulfuric acid for neutralization.[16]

Descroizilles found that the strength of some commercial alkalis used in France was as follows: (a) American pearl ash of the first quality, 60 to 63 degrees, (b) American pearl ash of the second quality, 50 to 55 degrees, (c) white Russian potash, 52 to 58 degrees, (d) white potash from Danzig, 45 to 52 degrees (e), Alicante barilla, 20 to 32 degrees, and (f) Egyptian natron, 20 to 33 degrees.

Descroizilles discussed in detail the possible problems and anomalies that could occur when using his alkalimeter, and ended his paper with a possible explanation for the origin of natural soda, and natron.[16] In a second part to this memoir he added information about the use of his alkalimeter in the new industries based on the Leblanc process.[17]

Concentration of sugar beet syrup

Several publications about the concentration of sugar beet juice had reported the appearance of NO_2 towards the end of the process and assumed that the gas originated from the decomposition of the nitrates assimilated by the beets from the fertilizers used during their cultivation. Descroizilles believed that this explanation was incorrect because it was hard to see how a nitrate could decompose during such a simple operation as evaporation.[35] The processing of the juice involved addition of quicklime to clarify the liquid, followed by addition of sulfuric acid to neutralize the base. Since the acid was added in excess, this excess was the one that acted upon the nitrates present in the juice and decomposed them by the action of heat.

In a footnote to Descroizilles's paper, Pierre Jean Robiquet (1780-1840), one of the editors of the journal, criticized Descroizilles's explanation indicating that the generation of NO_2 was also observed during the fermentation of sugar beet juice to which no quicklime or sulfuric acid had been added, and also during the fermentation of other plant juices. Robiquet believed that the gas originated from the reaction between organic substances and nitrates. A following paper by Tilloy, provided additional experimental evidence to justify Robiquet's explanation[36]: (a) a bunch of green absinth, collected only one day before, was put in an alembic, together with the required amount of water, to extract the essence. Evolution of NO_2 was seen as soon as the distillation began; (b) A Dijon merchant, having a stock of 10 tons of sugar beet, syrup had hired a pharmacist to find a way of fermenting this liquor and prepare a fruit brandy. The pharmacist added beer yeast and observed that CO_2 and NO_2 began to be released and that the fermentation stopped shortly thereafter. Assuming that this was caused by poor quality of the yeast, he added a new portion of fresh yeast, and observed the same results. After several unsuccessful trials, he abandoned the job. Tilloy bought a 25 kg sample and observed that it had a slight ammonia odor and contained a large amount of crystallized sugar. Before trying to ferment it, he added seven to eight times its weight of water and enough sulfuric acid to make the liquid acid, followed by addition of yeast. The fermentation process went on without problems and he obtained the same amount of fruit brandy he would have obtained from the best cane molasses. He bought a larger quantity of syrup from the merchant, repeated the process, and this time he noted generation of a large amount of NO_2, following by a termination of the fermentation process. He could not believe that this gas was generated by the reaction between sulfuric acid and a nitrate because the diluted syrup should have retained nitric acid in solution, without decomposition. He now bought 100 kg of syrup, diluted it with 200 kg of water and added a large amount of sulfuric acid to assure that this time the solution was decidedly acid. This time he noted the evolution of a very large amount of only CO_2. He then brought the liquid to boiling and did not observe the release of NO_2. After cooling the liquor, he added four times its weight of water, and yeast. The resulting fermentation went on without problems, without generation of NO_2, and produced the appropriate amount of fruit brandy.[36]

From these results Tilloy concluded that independently of the state of the syrup and its being slightly acid or alkaline, if it was first diluted with six or seven times its weight of water and then treated with yeast, the fermentation would stop some time after initiation of the NO_2 release. To avoid this problem, it was enough to add first to the syrup twice its weight of water, boil the solution for a short time, and then add to it three or four time of water, and three to four % of sulfuric acid. It was not possible to attribute to the acid the generation of NO_2, because it was not present in the first stage of the process.[36]

Disinfection with chlorine

In 1811 Louis-Bernard Guyton de Morveau (1737-1816) described the experiments, which had been done on the use of chlorine for the treatment of scarlet fever, pernicious fevers affecting prisoners, hydrophobia, scabies, and for disinfecting fumigations.[37] For example, in 1810 a disinfecting fumigation had been employed in the hospital of the Ramekens Fort, located in the isle of Walcheren (Holland), where Spanish prisoner soldiers were hospitalized or kept for working purposes. The basic procedure used was to place large earth pots containing a highly a diluted solution of chlorine in the rooms holding about 120 persons. Every morning, before departing for work, the occupants were required to wash their hands and mouth with this solution. Similar vessels were positioned in open spaces, in pits full with infected sludge, so that the workers were day and night submerged in an atmosphere of chlorine. Prisoners infected with scabies found prompt cure after several hand washes with the chlorine solution, or passing a wet cloth in the infected parts of their bodies.[37]

In a paper published the same year, Descroizilles reported that he had employed solutions of HCl for the same purposes, as a preventive measurement for workers working in earth removal particularly in marshes. Each worker was provided with a small glass vessel containing aqueous HCl and manganese black dioxide. The worker would position the vessel near him, in the direction of the wind; thus being subject to an individual fumigation (Descroizilles named then *fumigation Guytonnienes*). Descroizilles also provided each worker with an additional vessel filled with an aqueous solution of chlorine (Berthollet's bleach). Every half and hour or so, the worker would rub his hands with this solution for antiseptic purposes (Descroizilles named this process *Berthollienne frictions*).[14]

Fermentation of cider and pear brandy

Upon hearing that the 1822 crop of grapes and apples was to be very abundant, Descroizilles decided to publish an account of the experience he had accumulated on the subject for over 40 years.[38] He wrote that the shell life of wines depended more or less on the amount of fruit liquor formed or added to them; this content was easily determined by distilling one glass of wine with the portable still that Descroizilles had designed and offered for sale. Wines containing less than 18 to 19% volume of fruit alcohol were the most vulnerable. The origin of this low level was the fact that grapes collected in rainy or cold years contained a lower than average level of sugars. One was way of solving the problem was to increase the amount of sugar present in the fruit juices or add alcohol obtained from fruits. The second method was very expensive because of the distillation cost. Interesting enough, most people were not aware that most of the wines valued as cordials were a 1:1 mixture of non fermented juices of the best grapes grown in southern France and fruit liquors.

Descroizilles recommended that the conventional tubs used for fermenting cider and pear juice be replaced by large kegs (exposed to sunlight), as those normally used for transporting beverages, to minimize contact with air and facilitate elimination of the CO_2. In order to favor these processes, Descroizilles designed an artifact, which he named wine blower (*soufflé œnologue*); composed of a simple siphon, made of tin, having one end longer than the other by about 8 centimeters, and slightly closed at one end. The external end of the siphon was submerged in a bottle containing water. When the level of the broth rose due to frothing, the siphon allowed eliminating the excess CO_2, while avoiding entrance of atmospheric air and decreasing the discharge of small particles of the fruit. This allowed the operator a visual expression of the process occurring inside the keg. The grinding of the fruit could also be improved substantially by substituting the vertical grindstone by a serrated small cylinder similar to the one used to divide potatoes for extracting the starch. In his memoir Descroizilles gave a detailed description of the modifications to be made to all the equipment he suggested for improving the efficiency of the fermentation process, as well a making it more economical.[38]

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