Carl Wilhelm Scheele

Jaime Wisniak.

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105 mail to: wisniak@bgumail.bgu.ac.il

Recibido: 15 de septiembre de 2008. Aceptado: 20 de diciembre de 2008.

Palabras clave: oxígeno, cloro, glicerina, lactosa, ácido tartárico, cianuro de hidrógeno, fotografía.
Key words: oxygen, chlorine, glycerin, lactose, tartaric acid, hydrogen cyanhydride, photography.

RESUMEN. Carl Wilhelm Scheele (1742-1786), un científico con mínima educación formal y científica, llegó a ser uno de los más famosos químicos experimentales de todos los tiempos, descubriendo, aislando, y caracterizando una infinidad de elementos y compuestos inorgánicos y orgánicos, entre ellos, oxígeno, cloro, tetrafluoruro de silicio, arsenito de cobre, glicerina, lactosa, y los ácidos fluorhídrico, sulfhídrico, cianhídrico, tartárico, cítrico, láctico, úrico, benzoico, gálico, oxálico, arsénico, prúsico, molíbdico y túngstico. Fue el primero en observar el efecto de luz de diferentes longitudes de onda sobre las sales de plata (que formarían la base de la fotografía moderna). Scheele fue un fuerte partidario de la teoría del flogisto y la usó para explicar sus resultados experimentales, sin considerar otras posibilidades.

ABSTRACT. Carl Wilhelm Scheele (1742-1786) a scientist with little formal education and training in science, became one of the greatest experimental chemists of all times, discovering, isolating, studying, and characterizing a very large number of elements and inorganic and organic compounds, among them, oxygen, chlorine, silicon tetrafluoride, copper arsenite, glycerol, lactose, and the acids hydrofluoric, hydrogen sulfide, hydrogen cyanide, tartaric, citric, lactic, uric, benzoic, gallic acid, oxalic, prussic, arsenic, molybdic, and tungstic. He was the first to report the action of different light of different wavelength on silver salts (which became the basis of modern photography). Scheele was a strong believer in the phlogiston theory and based on it the explanation of his findings; he did not go further on other possible theories.

LIFE AND CAREER[1-5]

Carl Wilhelm Scheele was born in Stralsund, Swedish Pomerania, on December 19, 1742 and died in Köping, Sweden, on May 21, 1786. He was the seventh of eleven children (six boys and five girls) of Jochim Christian Scheele, a brewer and later broker, and Margaretha Eleonora Warnekros. Like his oldest brother, Johan Martin (1734-1754), Carl became interested on pharmacy at an early age and chose it as his career. It is said that while still a boy he was taught by two friends of the family in Stralsund, a physician named Schutte and a pharmacist named Cornelius. After finishing school, which did not include a Gymnasium course, Scheele went to Göteborg in 1757, at the of age 14, to began his training with Martin Anders Bauch, the owner of the pharmacy at the Unicorn in Gothenburg, taking the place of his brother Johan Martin, who had died of typhoid two years before. The stock of chemicals present in the pharmacy afforded Scheele with a starting point for many investigations and discoveries. His master promptly recognized the unusual abilities of his apprentice and encouraged him by putting at his disposal the necessary chemicals and equipment, as well as allowing him to use his well-equipped library. Three of the most famous chemical handbooks of the time, Johann Kunckel's (1630-1703) *Laboratorium Chymicum,*[6] the *Cours de Chimie* of Nicolas Lémery (1645-1715),[7] and Caspar Neumann's (1648-1715) *Prœlectiones Chemicœ*,[8] were available in Bauch's pharmacy: and Scheele undertook to repeat the numerous experiments in these books and acquire the preparative and analytical techniques, which later would be critical for his discoveries.[1-5]

Scheele remained with Bauch beyond his six years of apprenticeship, a year after qualifying as a joumeyman (skilled worker), until the pharmacy was sold in 1765.[3,4] Then he left Göteborg and for the next ten years traveled as a journeyman. In Malmö he found work as a clerk in the Pharmacy at the Spotted Eagle, owned by the pharmacist Peter Magnus Kjellström.[5] Kjellström understood Scheele's preference for experimental work and allowed him to work in the laboratory of the pharmacy. Equally important for his future career was his initial contact with the academic world, through Anders Jahan Retzius (1742-1821), another pharmacist, who was then an assistant teacher of chemistry at the nearby University of Lund and then returned to Lund in 1772 as director of the botanical garden. To Retzius goes the credit of having been the first real scientist to recognize and take advantage of the genius in the young apothecary clerk.[1,5]

Scheele stayed in Malmö for three years, until attracted by the better facilities available in Stockholm and its surroundings: the Royal Swedish Academy of Sciences and the university of Uppsala. In the spring of 1768 he took a position in the Stockholm Pharmacy at the Raven run by Johan Scharenberg, but there he was allowed only to prepare prescriptions. In the summer of 1770 he moved to the Pharmacy at the Arms of Uppsala, owned by the apothecary Christian Ludwig Lokk. There he had a workbench in the laboratory and was soon recognized as an able chemist. In Uppsala, Scheele met Johan Gottlieb Gahn (1745-1818), a former chemistry student of Torbern Olof Bergman (1735-1784) who occupied the chair of chemistry at Uppsala University. Gahn left Uppsala to work as a mining engineer at the Falun copper mine, and before so he introduced Scheele to Bergman.[1-5]

On February 4, 1775, still a studiosus pharmeciae, he was elected a member of the Swedish Academy of Sciences and began to publish in its *Handlingar* (Transactions).

In 1775 Scheele got his own pharmacy in the small town of Köping. Sara Margaretha Sonneman, the daughter of a councilman in Köping, had married the pharmacist Herman Pohl in 1712. After Pohl's death in 1775, she offered Scheele the management of the business; including the condition that he would run the pharmacy independently for one year and after nine months he could negotiate for its purchase. This arrangement was put to test very soon; a wealthy apothecary offered Sara such profitable price that she decided to sell the store. This was the first event in which Scheele's abilities proved to his benefit: In less than a year, he had become so popular and respected that the citizens of the province demanded that he continue to be the city's pharmacist. He remained in the small town until his death, disregarding all offers to leave it, including that to succeed Andreas Sigmund Marggraff (1709-1782) at Berlin.[1]

According to Urdang,[5] Adolf Erik Nordenskiöld (1832-1901), the mineralogist and polar scientist, described this event in Scheele's life as in the following words: *"Gahn offered Scheele a position as collaborator at Falun, in all probability to secure Scheele's advice in matters of a chemico-technical nature for the great industrial plants of that place. Bergman wanted him back at Uppsala. At the initiative of other friends of Scheele, among them Linné, Wargentin, the Secretary of the Royal Academy of Science, and the brothers Bergius, who were very influential in the scientific circles of Stockholm, the great Swedish industrialist P. Alstromer offered Scheele the pharmacy at Alingsas with an appropriate laboratory under favorable conditions. It was planned to make him manager of a distillery or, the most appropriate plan of all, to create for him the position as "Chemicus Regius" (Royal chemist) in the capital."*

As stated by Urdang[5] Scheele was proud in being a pharmacist. "It was not until 1777 that he found time to go to Stockholm to take the examination as a Swedish apothecary. Under the presidency of the physician in ordinary to the King of Sweden, Abraham Baeck, members of the Royal College of Physicians, with the assistance of two apothecaries, formed the examination board. They made the examination an act of reverence to the famous candidate. After receiving his certificate, Scheele designated himself an apothecary whenever he signed an official document. For his lecture before the Royal Academy of Science on the occasion of his initiation, he probably chose a pharmaceutical topic deliberately, the presentation of his new procedure of preparing calomel (mercurous chloride). The search for this process as well as for Scheele's new method of preparing algaroth powder (antimony oxychloride) was avowedly caused by his desire to present his colleagues with methods less harmful to their respiratory organs than the old ones".[5]

During his stay in Uppsala Scheele began his major work: to combine the many and varied experiments with fire and air made during the previous years into an integrated book, *Chemische Abhandlung von der Luft und dem Feuer* (Chemical Treatise on Air and Fire).[9] The main result was the proof that air consists of two elastic fluids, one of which supports combustion and calcination (fire air, oxygen), while the other (foul or vitiated air, nitrogen), does not. An interesting part of this experiment is the one related to the respiration process in living subjects, Scheele realized that lime removes *aer fixus* (carbon dioxide) from air and thus separates into its various components through physiological processes.[1]

Was Scheele or Joseph Priestley (1733-1804) the actual discoverer of oxygen? This question has been the subject of much discussion in the literature[1,2,10-15] and it probably originates from an unfortunate incident in the process of publication of Scheele's book. Scheele's correspondence and notebooks show that the manuscript was submitted to the printer (Swederus) in 1775 and that much of the experimental work reported in it was performed at beginning of Scheele's chemical career. The printing of the book was delayed for two years, partly because Bergman did not deliver his promised preface until July 1, 1777; the work appeared the following month, and carried a long introduction by Bergman, who said that he had repeated and confirmed many of Scheele's experiments. By the time of publication, oxygen was already known and others had published some of the observations in the book. In October 1774 Priestley informed Lavoisier of his discovery of a new remarkable gas on 1 August.[1]

Between 1768 and 1770, at about the same time as Priestley was beginning to work on gases, Scheele prepared, collected in bladder and examined some of the properties of fixed air (carbon dioxide) and studied the fumes (oxides of nitrogen) given out by volatile acid of nitre (nitre acid).[3] In his letter of August 2, 1774, to the secretary of the Stockholm Academy, Per Wilhelm Wargentin (1717-1783), he stated that he had studied air and fire for many years, and mentioned that until recently he had thought he was the only one to know of certain phenomena but that *"some Englishman had gone very far in his researches."* Scheele's manuscripts show that he isolated oxygen from several substances, including red mercury calx (mercuric oxide) at least two years before Priestley did so in a famous experiment on August 1, 1774. It is still quite certain that Scheele and Priestley were each ignorant of the other's work.[4] According to Smeaton3 Partington has shown that although Scheele's book did not appear until 1777, Bergman published an account of his discovery in 1774, probably before June 1774 and therefore three months before Priestley performed his experiment. There seems little doubt that the priority of both discovery and publication belongs to Scheele, and it is also certain that the two men worked independently.[3] Curiously, in a paper about a new type of air, until then unknown, read by Antoine-Laurent Lavoisier (1743-1794) in 1775 to the *Académie des Sciences* in Paris, he made no mention of Scheele or Priestley.[16]

Scheele died on May 21, 1786, at the age of forty-three. He suffered badly from rheumatism and gout; although the nature of his final illness is not known, it is very probable that it was related to a long-term exposure to highly toxic substances such as arsenic acid and hydrogen cyanide. As other chemists of his time, he practiced testing and smelling the different substances he prepared. Aware that he had only a few days to live he married Sara Pohl, thus ensuring that she would once again inherit the pharmacy.[5]

As a chemist Scheele was internationally known and respected, and during his lifetime his publications, which originally appeared in Swedish or German, were nearly all published in French and English translations. Many important foreign scientific societies appointed him honorary member, among them *Gesellschaft Naturforschender Freunde zu Berlin* (1778), *Regia Scientiarum Taurinensis Academia* (1784), *Societá Italiana* at Verona (1785), *Societé Royale de Médicine* at Paris (1785), and *Churmainzische Gesellschaft der Wisssenschaften* at Erfurt (1785).[5]

According to Boklund, Nordenskiöld was the first who tried to decipher and put order in Scheele's manuscripts. In connection with the commemoration of the 150th anniversary of Scheele's birth (1892) Nordenskiöld published a selection of Scheele's correspondence with excerpts from his laboratory notes. In 1942, in connection with the festivities held on the bicentennial of Scheele's birth, a new edition, edited by C.W. Oseen, of the laboratory notes from which Nordenskiöld had presented excerpts was published.[1]

While in Stockholm. Scheele also undertook research on the chemical reactions of light on silver salts and discovered that different parts of the solar spectrum reduce it with different strength. In his book on Air and Fire, when discussing the nature of light, he writes: *"The beautiful colors, which light continually shines, are proofs... that light cannot be phlogiston only...Place a glass prism...Place a piece of paper which is besprinkled with horn silver (the mineral form of silver chloride); it will be observed that (it) becomes black far sooner in the violet color than in the other colors; that is, the calx of silver separates the phlogiston sooner from the violet light than from the other colors...light cannot be looked upon as a simple substance"*.[9]

An interesting point of historical value is that in 1737, Jean Hellot (1685-1766), in his first memoir about invisible ink, wrote:[17] *"la dissolution de l'argent fin dans l'eau-forte, qu'on affaiblie ensuite par l'eau de pluie distillée...fait aussi une écriture invisible, qui tenuë bien enfermée, ne devient lisible qu'au bout de trois ou quatre mois; mais elle paroît au bout d'une heure si on l'expose au soleil, parce qu'on accélère l'évaporation de l'acide..."* (The solution of silver in aqua fortis, diluted afterwards with rain water...also makes an invisible ink, which kept in the dark des not become visible before three to four months, but appear within one hour if exposed to the sun because it accelerates the evaporation of the solvent). This result permits attributing to Hellot the discovery of the (global) photo sensibility of paper with silver nitrate, which would later be applied in the art of photography.[18]

SCIENTIFIC ACHIEVEMENTS[1,19-23]

Thomas Edward Thorpe (1845-1925) describes the achievements of Scheele as follows:[22] *"We owe to Scheele our first knowledge of chlorine, and of the individuality of manganese, and baryta.He was an independent discoverer of oxygen, ammonia, and hydrochloric acid gas. He discovered also among the inorganic acids hydrofluoric, nitrosulfonic, molybdic, tungstic, and arsenic, and among the organic acids, he discovered lactic, gallic, pyrogallic, oxalic, citric, tartaric, malic, mucic, and uric acid. He isolated glycerin and milk sugar; determined the nature of sodium ammonium phosphate, borax, and Prussian blue; and prepared hydrocyanic acid, demonstrated that plumbago is carbon associated with more or less iron;*[24] *ascertained the chemical nature of sulfureted hydrogen (hydrogen sulfide); discovered arsine, and the green arsenical pigment which is associated with his name (Scheele's green or copper arsenite). He invented new processes for preparing ether, powder of algaroth (antimony oxychloride), phosphorus, calomel, and magnesia alba (calcium carbonate)."*

Scheele's discovery of molybdic acid in 1778 led to the isolation of metallic molybdenum by Hjelm (1782); and his discovery of tungstic acid in 1781 paved the way for the isolation of metallic tungsten by the Spanish brothers Juan José and Fausto d'Elhuyar (1783) (From Swedish, *tung* = heavy and *sten* = stone), which superficially resembled graphite. The mineral, calcium tungstate, $CaWO_4$, was eventually named Scheelite).[25]

Fluorspar

Scheele's first independent publication[26] described his investigation of fluorspar (calcium fluoride)..."*a remarkable kind of stone, especially on account of its beautiful phosphorescence in a dark room on heating it...But its constituents...(are) less known hitherto.*"He studied its behavior with acids (sulfuric, nitric, hydrochloric, phosphoric, and fatty acids), alkalis (sodium and potassium hydroxide), and salts (ammonium chloride, sodium sulfate, mercurous chloride, mercuric sulfate, etc.). He showed that when treated with oil of vitriol (concentrated sulfuric acid) it yielded a volatile acid (hydrogen fluoride, Swedish acid), which attacked glass and reacted with water to form silica (silicon dioxide). Scheele thought at the time that the silica was an essential component of the volatile acid, but he later confirmed the experiments of the apothecary Johann Friedrich Meyer (1705-1765) showing that silica was not deposited from the new acid if it was prepared in an iron retort.Scheele proved that the silica in his acid originated from the glass of the reaction vessel: *"In order to convince myself also of this fact I ground pure fluorspar to powder...mixed it with oil of vitriol and put the mixture on a cast tin retort...provided with a receiver containing water and coated inside with wax... After an hour found the water very acid and fuming with no siliceous earth upon it...I repeated the experiment adding some rock finely ground crystal...the water (in the receiver)...(was now) quite thick from the silex (silicon dioxide) carried over and volatilized...Who does not see here then that the earth in the ordinary acid of fluorspar is only accidental and is derived from the siliceous earth in the glass retort?*[4,19]

Manganese

When the experiments on fluorspar were finished, Bergman suggested that Scheele study the chemistry of pyrolusite, (impure manganese dioxide), sometimes-called black manganese or *black magnesia*. According to Scheele the varieties of manganese had attracted the attention of chemists for many years but they had discovered little more than those properties that served to differentiate them.[27] Scheele studied the solubility of pyrolusite under various conditions, in inorganic and organic acids, and concluded that the volatile acid of sulfur, the phlogisticated acid of nitre, the ordinary acid of salt, and the acid of lemons, dissolve it completely; others gave rise to noticeably effervescence during the dissolution, others dissolved it quietly, and others dissolved it only partially. Manganese had a strong attraction for phlogiston, which increased in the presence of solvents. After manganese had become with the inflammable principle, it lost its black color and acquired a white one. Since Scheele had shown that phlogiston was necessary for solution to occur, it could only have been derived from the heat that was supplied: *"Manganese can thus, with the aid of concentrated acid of vitriol, attract to itself from heat the phlogiston, which is required for its dissolution…the inflammable principle in acid of vitriol (if indeed this acid contains any such thing) contributes nothing to this solution."* According to Smeaton[3] this was Scheele's first published statement that heat was a substance containing phlogiston, a theory that he developed in his *Treatise on Air and Fire*.[9]

The most significant result were that pyrolusite reacted with spiritus salis to form a new gas (chlorine, which Scheele did not identify as a new element), which he described carefully and believed to be muriatic acid less hydrogen (see below); and that it contained a very small amount of a substance resembling lime but differing from it in some important properties, which he named heavy earth (baryta, barium carbonate).[1,4,28] Baryta, like the other earths, was regarded as an element until Davy and Jöns Jacob Berzelius (1779-1848) decomposed it by electrolysis around 1808.[3,29,30]

Chlorine[31,32]

Chlorine was the first of the halogens to be discovered and identified, although it was probably prepared a long time before, without knowledge of its nature. The treatise *Alchimia Geberi*, written by the Arab alchemist Geber in the thirteenth century or afterwards, contains a description of a procedure for preparing nitric acid by distilling a mixture of saltpetre, cupric sulfate, and clay, and the comment that the product is a more active solvent if some sal *ammoniacus* (ammonium chloride) is mixed with the ingredients. From this information we learn that Geber knew how to prepare *aqua regia* and that the corrosive, suffocating, greenish-yellow fumes of chlorine must have been known from the thirteenth century on by all the alchemists. Early in the seventeenth century Johannes Baptiste van Helmont (1579-1644) mentioned that when *sal marin* (sodium chloride) or *sal ammoniacus* and *aqua chrysulca* (nitric acid) were mixed together, a *flatus incoercible* (non-condensable gas) was evolved. It is also very probable that Johann Rudolf Glauber (1604-1668) obtained a similar gas by heating zinc chloride and sand; he wrote that by distilling spirit of salt with metal oxides, he obtained in the receiver a spirit the colour of fire, which dissolved all the metals and nearly all minerals. This liquid was no doubt chlorine water, which Glauber called *rectified spirit of salt* and said that it could be used for making many products useful in medicine, in alchemy, and in the arts. He illustrated his claim by pointing out that treating spirit of salt with alcohol furnished oleum vini, which was very agreeable and an excellent cordial.[32]

The meaning of these and other observations became understood after Scheele published his De Magnesia Nigra in 1774.[27] Scheele found that heating hydrogen chloride with manganese dioxide (pyrolusite) released a yellowish-green gas that smelled like warm aqua regia. In section 6 of his paper he describes the action of hydrochloric acid upon manganese dioxide as follows:[19] *"On one-half ounce finely ground Braunstein (pyrolusite) was poured one ounce of pure spiritus salis (hydrogen chloride). After this mixture had been standing in the cold for one hour, the acid had assumed a dark brown colour. One part of this solution was poured into a glass, which was placed over the fire. The solution gave off an odour like warm aqua regia and after one-quarter's hour duration, she was as clear and colourless as water, and the smell had disappeared. The rest of the brown solution was digested in order to see whether the salt acid would become saturated with the braunstein. As soon as the mixture grew hot its smell of aqua regia became considerably stronger; effervescence ensued which continued until the next day, when the acid became saturated. One ounce of spirit salis was again poured upon the undissolved residuum, whereupon all the above-mentioned phenomena followed and the braunstein was almost entirely dissolved, except for a small amount of siliceous earth"*.

Scheele concluded his study with the following statement (section 13):[19] *"Before I enter into an explanation of these peculiarities, it will be necessary to give an account of the general properties of braunstein...Braunstein has a strong attraction for all phlogistic substances. This attraction becomes stronger when a menstruum present which at the same time can unite with the phlogisticated braunstein. When braunstein is saturated with phlogiston it loses its black appearance and acquires a white color; the black color, however, reappears as soon as the phlogiston separated from it again. There is no way of producing a colorless solution of braunstein without combining it with phlogiston. By means of these four general properties of braunstein, discovered by a series of experiments, all its known reactions can easily be explained."* The following eleven sections of the paper describe the action of sulfuric acid (acid of vitriol), nitric (acid of nitre), uric (acid of urine), tartaric (acid of tartar), acetic (distilled vinegar), citric (acid of lemons), fluorhydric (acid of fluorspar), and aerial (carbon dioxide) acids. Then (section 23), he gives a much more detailed description of the experiments with hydrogen chloride: *"It does not immediately appear whence braunstein has obtained phlogiston; nothing combustible is added here and nevertheless the complete dissolution can be effected without heat. In fact, a phenomenon takes place that here proves that phlogiston is certainly present in the acid of the salt…when the acid stood over braunstein in the cold; it acquired a reddish brown color. As braunstein does not give any colorless solution without uniting with phlogiston, it follows that the acid of salt can dissolve it without this principle…Braunstein as here attached so loosely to the salt acid that water can precipitate it and this precipitate behaves like ordinary braunstein. Whenever I exposed the mixture of braunstein and spiritus salis to digestion, effervescence ensued with a smell of aqua regia. In order understand this novelty clearly, I took a retort containing a mixture of braunstein and acidum salis…tied to its neck an empty bladder and put it in hot sand. The bladder became expanded by the effervescence in the retort. When the acid no longer effervesced, which was a sign of its saturation, I removed the bladder and found that the air produced had rendered it as yellow as aqua regia would have done, but did not contain any fluid air; it had a very perceptible suffocating smell, highly oppressive to the lungs, and resembling that of warm aqua regia. The solution remaining in the retort was clear and of a yellowish hue; which was owing to the iron contained in it."* To Scheele, these results were a clear indication that braunstein had combined with phlogiston, leading to the critical question and the clear cut answer to it: *"But whence has this braunstein acquired its phlogiston? From the acidum salis. The matter of heat has no share here, because the solution becomes clear without it, only it must stand several hours in the open air. Change takes place in the solution in the following manner: the acid of salt, whence a brown solu-*

tion arises, first attracts the braunstein. The braunstein thus dissolved acquires by means of the acid a strong attraction for phlogiston, and actually withdraws it from the particles of the acid with which it is combined (becoming dephlogisticated salt acid) *These particles having thus lost one of their constituent parts, and being but very loosely combined with the phlogisticated braunstein, are expelled from it by the remaining salt acid, which has not yet suffered any decomposition, and appear with an effervescence as a highly elastic air, or similar fluid. The brown color was now disappeared and the solution become clear as water".*

Scheele went on to describe the properties of the new gas and the procedure for doing so:[19] *"In order to investigate the properties of this air it is best to put it in the elastic state. Ordinary acid of salt is mixed with finely ground braunstein, as much as desired, in a glass retort, which is put into warm sand, Small glass bottles, capable of containing about twelve ounces of water, are employed as receivers. About two drachms of water are put into each bottle and the joints are luted* (made air tight) *by tying a piece of blotting paper round the neck of the retort and fixing the bottle upon this. In a quarter of an hour or a little longer a quantity of the elastic fluid going over into the receiver gives the air contained in it a yellow color; the bottle is then removed from the retort. If the paper luting has held fast, a portion of the aerial fluid will rush out with force. A previously fitted cork immediately closes the bottle, and another one is attached to the neck of the retort. In this way several bottles can be partially filled with dephlogisticated acid of salt. In the process care should be taken to fix the retort in such a position that if any liquid condenses in the neck it may run back. The water put into the bottles serves to condense the vapors of salt acid should any go over. I fill several glasses at once in order to get a good quantity, and to avoid the trouble of repeating the process as often as I want some of the fluid for my experiments. It is better to make use of small vessels for receivers, because if one large one is used, a good deal of the substance is lost every time the cork is taken out. The bodies which I wished to expose to the action of this dephlogisticated salt acid I hung on a glass tube, which I fastened to the cork".*

With gas thus prepared Scheele discovered many of the notable properties of chlorine:[19] (a) The corks of the bottles became yellow, as if from aqua fortis, and during the distillation the luting was likewise attacked. (b) Blue litmus paper became almost white; all vegetable flowers, red, blue and yellow, became white in a short time; the same thing also occurred with green plants. In the meantime the water in the bottle became changed to a weak and pure acid of salt. (c) The former colors of these flowers, as well of that of the green plants, could not be restored either by alkalis or by acids. (d) Expressed oils and animal fats, when they hung as drops, or were rubbed, upon the glass tube, became in a short time as tough as turpentine. Scheele noticed further, that cinnabar, vitriol of iron, iron fillings, and all metals were attacked, and that that the solution of gold in this dephlogisticated acid of salt formed fulminating gold with volatile alkali (ammonia). In addition, (i) *"when spirit of ammonia, hangs in drops upon a tube, a white cloud arose…. and a great number of air bubbles escaped, which gave off smoke when they burst asunder…(k) Fixed alkali was converted into common salt, which decrepitated on charcoal but did not detonate. (l) Arsenic deliquesced in these vapors. (m) Insects immediately died in them, and (n) a flame was instantly extinguished by them".*[19]

According to Partington[2] the phlogiston theory, prevalent at Scheele's time, led him to assume that in the presence of acids the manganese ore readily took up phlogiston and dissolved in water. Consequently, the new gas was thought to be muriatic acid freed from hydrogen (then believed to be phlogiston) and named *dephlogisticated muriatic acid*. An interesting fact is that at the time of the discovery of chlorine Scheele was only thirty years of age and was working for the apothecary Lokk at Uppsala.

It was left to Humphry Davy (1778-1819) to prove unequivocally that chlorine was an element.[33,34] In his *Researches on the Oxymuriatic Acid*[31] Davy described his unsuccessful attempts to decompose oxymuriatic acid gas. He found that heating dried muriatic acid with metallic sodium or potassium, yielded metallic muriate and hydrogen, but no water or oxygen, indicating that no oxygen was present in either muriatic acid gas or oxymuriatic acid gas. The reaction of potassium with muriatic acid produced more than one third of its volume of hydrogen.

According to Schultze[35] the discovery of chlorine was destined to exert a profound influence in the development of civilization. In time, *"chlorine would grow to become one of the most versatile commodities, finding its way into hundreds of applications and products beneficial to the health, comfort, and enjoyment of people throughout the world."* These goals were not achieved easily; they had to wait solving problems related to the high corrosiveness of wet chlorine, its supply in a concentrated form, and production from easily available materials, at an appropriate cost. In the beginning, most production facilities were based on variations of Scheele's method, that is, reacting hydrogen chloride with manganese dioxide

$$MnO_2 + 4HCL \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

a reaction carried at 100 to 110 °C . As discovered later, reaction 1 actually took place in two steps; in the first one manganese tetrachloride was formed, which then decomposed into manganese dichloride and chlorine.

Arsenic

Arsenic had been known for a long time, it was known to form with pure metals or their alloys, fusible alloys colored like silver or gold. In 1746 Pierre Joseph Macquer 1718-1784) distilled the reaction product of arsenic oxide (white arsenic) with potassium nitrate and found that the residue consisted of the salt of potassium and a particular acid originating from arsenic (potassium arsenate), The same results were obtained using potassium and calcium hydroxide (These arsenates are known as Macquer's salts), Macquer described these salts in details but did not go further into the matter.[36] In his experiments on manganese[27] Scheele had found that inflammable matter was not only found in arsenic but could actually be separated from it. Hence, he asked himself the question: What might the remainder of the arsenic be?[37] He subjected arsenic oxide to the action of nitric acid and manganese and obtained a material, which he named *acid of arsenic*. Before using it in other experiments he examined if it was equally fatal as arsenic itself. He mixed a little in honey and placed before flies: these died one hour afterwards. He then studied the behavior of the acid of arsenic with inflammable substances such as charcoal (no change, except if heated very strongly), oil of turpentine, fatty acids, sugar, sulfur, and spirit of wine. The mixture with sulfur did not react during digestion, but evaporated to dryness and then distilled, a violent combination took place that heated the mixture to the melting point of sulfur. Scheele concluded that the acid of arsenic sublimed with sulfur formed red arsenic and a volatile spirit of sulfur. The following experiments studied the behavior of arsenic with salts of the alkalis, ammonia, gypsum, heavy spar, fluorspar, lime, magnesia alba (magnesium carbonate), earth of alum (argil), clay, silicon oxide, and metals such as gold, platinum, silver, mercury, copper, iron, lead, tin, zinc, bismuth, antimony, cobalt, and manganese. The reaction with copper produced a green colored solution of acidic copper arsenite ($CuHAs_3$), which became known as *Scheele's green*. This compound was used for many years; by the end of the 19th century it had replaced the older green pigments based on copper carbonate, until it was abandoned on account of its poisonous nature. The Swedish Academy of Science requested from Scheele to publish a detailed description of his green, and this he did in 1778.[38] The procedure consisted in dissolving cupric sulfate in hot water followed by addition of an aqueous potassium hydroxide and white arsenic. The precipitated copper arsenite was filtered and dry by heating.

Molybdenum

The Swedish mineralogist Alex Fredrik Cronstedt (1702-1765, the discoverer of nickel) described a black mineral, *molybdaenœ membranacea nitens*. In 1754 B. A. Quist obtained from it a white powder, which he thought to be a calx (oxide) of tin. Quist found the mineral to be almost completely volatile in the open fire and to contain sulfur. In 1778 Scheele digested samples obtained from different sources with all known mineral acids and found that only by acids of arsenic and nitric acid attacked it. The nitric solution was evaporated to dryness and treated with nitric acid several times until a chalk-white powder of acid nature, was obtained, with Scheele named *terra molydœnœ* (MoO_3). He tried unsuccessfully to reduce it to a metal, with black flux and charcoal, and with borax and charcoal; he also observed that the earth gave a blue solution with hot concentrated sulfuric acid, that became thick after cooling. He concluded that the *"earth is not predisposed to attract phlogiston as shown by the blue color which its sublimate acquires from the candle flame"* and that it is probably the calx of an unknown metal but unlike other calxes, which react only with acids, this also reacts with potash and forms a salt.[39]

Organic chemistry

Many chemists had tried to crystallize citric acid by evaporation, without success. Scheele believed that the failure was due to the presence of impurities that hindered the process. To overcome the problem, he first heated clear lemon juice to its boiling point, followed by addition of chalk (limestone) under continuous stirring, and then let the mixture cool, upon which lime saturated with acid of lemons (*calx citrata*) settled on the bottom as heavy powder. The powder was washed with water several times and then treated with diluted sulfuric acid. The calcium sulfate precipitate was separated by filtration and the clear filtrate until it crystallized in small crystals.[38] In additional papers Scheele reported his experiments on the separation of the acids present in a wide variety of fruits and berries, such as gooseberry, sour apples, cranberry, red whortleberry, bird cherry, plum, currants, raspberries, grapes, etc., as well in substance of vegetable or animal origin, such as gum arabic, milk sugar, starch, aloe, cinchona, rhubarb, opium, galls, white of egg, yellow of egg, urine, and blood. He thus succeeded in isolating organic acids such as tartaric, mucic, pyromucic, uric, hydrocyanic, oxalic, citric, malic, gallic, pyrogallic, and lactic acid, by precipitating the acid as an insoluble calcium salt or potassium ferrocyanide and then separating it with diluted sulfuric acid.[41,42]

Scheele also developed a process for preparing Prussian blue and obtaining prussic acid (hydrogen cyanide) from it.[43]

In 1783 Scheele investigated the sweet principle present in oils and fats obtained by expression, which appeared when the oils were boiled with calx of lead and water (a saponification process).[44] Apothecaries used the solid product obtained from olive oil to prepare a plaster known as *emplastrum simplex*. Scheele recognized that the solid precipitate was a kind of soap and that the supernatant liquid had a sweet taste. Scheele showed that this peculiar saccharine principle (glycerol) could be obtained from other oils and fats, such as oil of almonds, rape, and linseed. He evaporated the sweet substance to a proper consistency and noted that although it stood for several months in a cold place it did not crystallize. Evaporation of the concentrated liquid produced first a distillate of water and then another of the sweet principle. Further heating decomposed the residue into a brown vapor, which after condensation yield a black liquid of bitter taste and very penetrating smell (acrolein). In Michel Eugéne Chevreul (1786-1889) purified and analyzed the sweet principle and demonstrated it was glycerin.[45]

Urinary calculi[46]

The composition of urinary stones and calculi had occupied scientists for many years. Many famous chemists, such as Basilius Valentine, Paracelsus (1493-1541), and Jan Baptiste Helmont (1577-1644), and others had tried unsuccessfully to analyze urinary calculi. In 1776 Scheele collected calculi from various persons of both sexes who had been afflicted with calculary pain, ground the material, and subjected the powder to the action of water, sulfuric, nitric, and hydrochloric acid, and aqua regia. Only the last two dissolved the calculi when heated. The stones were slightly soluble in water and the diluted solution colored litmus paper red. The resulting yellow solution was acid and produced deep red spots when applied on the skin. The stones melted in alkali and formed a precipitate in acid solution, which dissolved in a hot nitric acid leaving a residue, which after evaporation turned a pinkish crimson. Upon heating, and depending on the temperature, it smelled like prussic acid, ammonia, or something like burning horn. Scheele named the substance *concrete acid* (lithic acid); subsequently others changed the name to *uric acid*. The solution obtained with hydrochloric acid or aqua regia was not precipitated when treated with earth of heavy spar dissolved in hydrochloric acid, by alkalis, and metallic solutions. Limewater decomposed the solution, producing a white precipitate that dissolved in hydrochloric and nitric acid. From these results Scheele concluded that the calculus was not of the nature of lime or gypsum but consists of an oily, dry, volatile acid, united with some gelatinous matter. In addition, all urine contained animal earth or lime, united with acid of phosphorus and a previously unknown concrete acid or calculus. He concluded his paper indicating that the urine of sick persons is more acid and contains more animal earth than of the health.[47]

Afterwards, Bergman confirmed Scheele's findings. Scheele's results are important because they established that uric acid was a normal constituent of human urine and that when cold it produced brick-red sediment. Thus uric acid became the first metabolite to be identified in human urine, twenty years before Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829) isolated urea in 1799.[48,49] Since most stones contained uric acid Scheele reached the wrong conclusion that uric acid was its only constituent.

Oxygen

The passages, quoted below, on the discovery of oxygen, are from the translation of Leonard Dobbin.[19]

According to Scheele, *"the investigation of the air is an all-important object of chemistry at the present time. This elastic fluid is endowed, too, with so many special properties that it can furnish material enough for new discoveries to anyone who takes such experiments in hand. Fire, this product of chemistry which is so wonderful, shows us that it cannot be generated without air…this treatise is only…an attempt towards a chemical theory of fire, that an existent in our atmosphere is to be regarded as a true constituent of fire and consequently contributes materially to flame; wherefore I have named this air fire air?*

Hitherto chemical investigators…hold that there remains no further hope of searching out the elements of substances…Others believe that earth and phlogiston are the things from which all material nature has derived its origin…(Without) fire…it is (impossible) to make any experiment; and without fire and heat it is not possible to make use of the action of any solvent…one (cannot) not form any true judgment regarding the phenomena, which fire presents, without a knowledge of the air...air really enters into the mixture of fire, and with it forms a constituent of flame and of sparks… The air…is also mixed with another elastic substance resembling air, which differs from it in numerous properties, and is…called aerial air by Professor Bergman. It owes its presence to organized bodies, destroyed by putrefaction or combustion… Nothing has given philosophers more trouble…than…this delicate acid or so-called fixed air…they believe that the air is in itself unalterable; and unites with substances thereby losing its elasticity; but that it regains its original nature as soon as it is driven out of these by fire or fermentation. But since they see that the air so produced is endowed with properties quite different from common air, they conclude…that this air has united with foreign materials, and that it must be purified from these admixed foreign particles by agitation and filtration with various liquids…Substances which are subjected to putrefaction or to destruction by means of fire diminish, and at the same time consume, a part of the air… Air must be composed of elastic fluids of two kinds…" Scheele now describes the series of experiments he performed to prove this point, for example, putting air in contact with an aqueous solution of potassium sulfide or a burning candle in a closed bottle and noting the decrease in volume. His first conclusion is that *"…phlogiston…is present in each of them…It is known that the air strongly attracts to itself the inflammable matter of substances and deprives them of it… it is evident that on the transference of the inflammable matter to the air a considerable part of the air is lost… the inflammable substance alone is the cause of this* action…*a given quantity of air can only unite with, and at the same time saturate, a certain quantity of the inflammable principle…air consists of two fluids differing from each other, the one of which does not manifest in the least the property of attracting phlogiston while the other, which composes between the third and the fourth part of the whole mass of the air, is peculiarly disposed to such attraction…Experiments that prove that ordinary air, consisting of two kinds of elastic fluids, can be compounded again after these have been separated from each other by means of phlogiston…Since this air is necessarily required for the origination of fire, and makes up about the third part of our common air, I shall call it…Fire Air; but the other air which is not in the least serviceable for the fiery phenomenon, and makes up about two thirds of our air, I shall designate after this with the name already known, of Vitiated Air."*

He now describes several experiments that allowed him to prepare fire air, for example, distilling a mixture of finely pulverized manganese with one part of the phosphorous acid of urine, distilling mercury nitrate… *"Whence comes the boiling of fused red-hot nitre…neither smoke nor vapors are seen to rise from it and yet coal dust flying above the open crucible takes fire, burning brilliantly…Mercury converted into calx by the acid of nitre, or red precipitate, (yielded) pure fire air, without any aerial acid in it"* Scheele used a bladder to collect the fire air coming over.

"I have mentioned…that I found vitiated air lighter than ordinary air. Must it not follow from this that fire air is heavier than our air?…I actually found that this was almost two grains heavier than the same bulk of common air.

"These experiments show...that this fire air is just that air by means of which fire burns in common air; only it is there mixed with a kind of air which seems to possess no attraction at all for the inflammable principle, and this it is which places some hindrance in the way of the otherwise rapid and violent inflammation…if air consisted of nothing but fire air, water would surely render small service in extinguishing outbreaks of fire air with 4 parts of aerial acid; in this mixture a candle still burned moderately well…It is a remarkable circumstance that the fire air…previously removed from the mercury its phlogiston in a slow calcination gives this same phlogiston up to it again when the calx is simply made red-hot."

"I placed a few flies in a bottle into which I had put some honey…After a few days they had died…I placed some peas in a small flask…and poured so much water upon them that they were half covered with it; I then closed the flask. The peas began to strike roots and grew up…after 14 days that they would not increase further. I opened the flask inverted, under water, and found the air neither increased nor diminished. The fourth part, however, was absorbed by milk of lime, and the remaining air extinguished flame. I kept fresh roots fruits, herbs, flowers, and leaves, each by itself, in the flask and after a few days I likewise observed the fourth part of the air converted into aerial. If flies are placed in such air they die immediately…These are accordingly strange circumstances, that the air is not noticeably absorbed by animals endowed with lungs, contains in it very little aerial acid, and yet extinguishes fire. On the other hand insects and plants alter the air in exactly the same way, but still they convert the fourth part of it into aerial acid…Hence

it is the fire air, which is…converted into aerial acid…I believe that one must ascribe to the blood present in the pulmonary veins, the effect which animals endowed with lungs have upon the air…in the open air assumes a fine red on the surface, and that the under portions likewise become red when they come into contact with the air. Does the air in this case undergo any alteration? I filled a flask one-third pan w*ith freshly drawn ox blood, closed it tightly with a bladder and shook up the blood frequently. Eight hours afterwards I neither found aerial acid in this air nor that its bulk was diminished: but the flame of a candle was immediately extinguished in it.*

“Plants…will not grow noticeably in pure fire air. I filled with this air a bottle…which contained 4 peas...They got roots, but did not grow up at all…There is no doubt that the whole quantity of fire air could have been converted to aerial acid if I had continued the operation longer…Hence it is the fire air by means of which the circulation of the blood and of the juices in animals and plants is so fully maintained. …I am inclined to believe that fire air consists of a subtle acid substance united with phlogiston and it is probable that all acids derive their origin from fire air. …If plants abstract the phlogiston from the air, the aerial acid must be lighter. But experiment shows me the opposite…Why do not blood and the lungs likewise convert fire air into such an aerial acid? Phlogiston, which makes most substances with which it unites liquid as well as mobile and elastic, must have the same effect upon blood. The globules of blood must attract it from the air through the small pores of the lungs. By this union they become separated from one another and are consequently made more liquid. They then appear bright red. They must, however, give this attracted phlogiston up again during the circulation, and in consequence, be placed in a condition to absorb the inflammable substance anew from the air at that place where they are in the most intimate contact with it, that is in the lungs…(Scheele is giving here a very reasonable description of the respiration process).”

“Water has the peculiar property of separating the proximate constituents of air; of uniting with fire air; and of entering into no kind of union with vitiated air” (Scheele is describing the now known fact that oxygen is more soluble than nitrogen in water). This fire air, dissolved in water must be as indispensable for aquatic animals as for those, which live upon the earth.

In the last chapter of his book, *Stinking sulfureous air*, Scheele describes his experiments on heating sulfur with different substances, such as lime, pyrolusite, alkali, charcoal powder, etc., collecting the gas generated in an empty bladder, and noting that sometimes it was vitiated air and in others, stinking sulfurous air (hydrogen sulfide). He concluded that the latter appears to be a compound of heat, phlogiston, and sulfur.

BIBLIOGRAPHIC REFERENCES

1. Boklund U, Scheele Carl Wilhelm, in Dictionary of Scientific Biography, 16 vols. C. C. Gillespie, Editor-in-Chief, Scribner, New York: 1970-1980.
2. Partington JR. A History of Chemistry, vol. 3, Mac Millan, London: 1962:p.493-516.
3. Smeaton WA, Carl Wilhelm Scheele (1742-1786), Endevour. 1986;10:28-30.
4. Smeaton WA. Carl Wilhelm Scheele (1742-1786), Provintial Swedish Pharmacist and World-Famous Chemist, Endevour. 1992;16:128-131.
5. Urdang G. The Apothecary Chemist Carl Wilhelm Scheele – A Pictorial Biography, Am Inst Hist Pharm, Madison: 1958.
6. Kunckel J. Laboratorium Chymicum, Hamburg: 1722.
7. Lémery N. Cours de Chymie Contenant la Manière de Faire les Operations qui sont en Usage dans le Mèdecine, Paris, 1675. Translated as A Course of Chemistry by Walter Harris, London: 1677.
8. Newmann C. Prælectiones Chemicæ, Zimmermann, Berlin: 1740.
9. Scheele CW. Chemische Abhandlung von der Luft und dem Feuer (Chemical Treatise on Air and Fire), Nebst einem Vorbericht von Torbern Bergman, Bokförlaget Rediviva, Stockholm: 1970:p.1777.
10. Boklund U. Carl Wilhelm Scheele - His Work and Life, The Brown Book, Roos Boktryckeri AB, Stockholm: 1968.
11. Cassebaum H, Magdeburg E. Pharmazie. 1974;29:603-607.
12. Cassebaum H, Schuffle H. Scheele’s Priority for the Discovery of Oxygen, J Chem Educ. 1975;52:442-444.
13. Kohl F., Carl W. Scheele – Discoverer of Oxygen, Pharm Ztg. 1992;137:48-50.
14. Partington JR. The Discovery of Oxygen, J Chem Educ. 1962;39:123-125.
15. Weeks ME, Leicester HM. Discovery of the Elements, 6th ed., Easton, J Chem Educ. 1956;168-171.
16. Laurent TC. What did Carl Wilhelm Scheele Look Like? Chem Intelligencer. 1999;July: 28-30.
17. Hellot J. Sur un Nouvelle Encre Simpatique. Part I, Mém Acad Roy Sci. 1737 (Published 1740);54-58:101-120.
18. Wisniak J. Jean Hellot – A Pioneer of Chemical Technology, Revista CENIC Ciencias Químicas. 2009;40:111-121.
19. Dobbin L. The Collected Papers of Carl Wilhelm Scheele, G. Bell, London: 1931.
20. Nordenskiöld AE. Carl Wilhelm Scheele, Efterlemmade Bref och Antechningar, P.A. Norstedt & Sons: Stockholm: 1892.
21. Oseen CW. Carl Wilhelm Manuskript 1756-1777, Tolkning, Royal Swedish Academy of Science, Uppsala, 1942.
22. Thorpe TE. History of Chemistry, in 2 vols. G.P. Putnam & Sons: London: 1909-1910.
23. Zekert O. Carl Wilhelm Scheele - Gedenkschrift zum 150 Todestage, Springer, Wien: 1936.
24. Scheele CW. Försök med Blyerts Plumbago, Kong. Vetenskaps Acad. Handlingar. 1779;40:238-245.
25. Scheele CW. Tungstens Beståndelar, Kong. Vetenskaps Acad. Nya Handlingar. 1781;2: 89-95.
26. Scheele CW. Undersökning om Fluss-Spat och dess Syra, Kong. Vetenskaps Acad. Handlingar. 1771;33:128-138.
27. Scheele CW. Om Brumsten, eller Magnesia, och dess Egenskaper, Kong. Vetenskaps Acad. Handlingar. 1774; 35: 89-116, 177-194.
28. Scheele, Chemical Examination of the Earth of Heavy Spar, Beschäftigungen Berlin. Gess. Natur. Freunde. 1779;4: 611-613.
29. Berzelius JJ. Pontin, Electrisch-Chemische Versuche über die Zerlegung der Alkalien under der Erden. Gilbert Annal. 1810;36:247-280.
30. Davy H. Electrochemical Researches on the Decomposition of the Earths, with Observations on the Metals Obtained from the Alkaline Earths and on the Amalgam Procured from Ammonia, Phil. Trans. 1808:333-370.
31. Chattaway FD. The Discovery of Chlorine by Scheele, Chem News. 1910;101:25-26.
32. Wisniak J. The History of Chlorine – From Discovery to Commodity, Indian J Chem Technol. 2002;9:450-463.
33. Davy H. Researches on the Oxymuriatic Acid, its Nature and Combinations; and on the Elements of the Muriatic Acid. With Some Experiments on Sulphur & Phosphorus, Made in the Laboratory of the Royal Institution, Phil. Trans. 1810;100,Part 2: 231-257.
34. Davy H. On a Combination of Oxymuriatic Acid and Oxygen Gas, Phil Trans. 1811;101:155-162.
35. Schultze HW. The Chlorine Industry – Past, Present, and Future, in Chlorine Bicentennial Symposium, T. C. Jeffery, P. A. Danna, and H. S. Hodel, editors, The Electrochemical Society, Inc., Princeton, New Jersey: 1974:pp.1-19.
36. Macquer PJ. Recherches sur l’Arsenic. Mém Acad Roy Sci., 1746 (Published 1751):223-237; 1748 (Published 1752):35-80.
37. Scheele CW. Om Arsenic och dess Syra, Kong. Vetenskaps Acad. Handlingar. 1779;37:89-116, 265-294.

38. Scheele CW. Method of Preparation of a New Green Color, Kong. Vetenskaps Acad. Handlingar. 1778;39:327-328.
39. Scheele CW. Försök med Blyerts Molibdæna. Kong Vetenskaps Acad Handlingar. 1778;39:247-255.
40. Scheele CW. Observations on Lemon Juice and on the Method of Crystallizing it. Kong Vetenskaps Acad. Nya Handlingar. 1784;5:105-109.
41. Scheele CW. Om Mjölk-sacker Syra Beståndelar, Kong. Vetenskaps Acad. Nya Handlingar. 1780;1:269-275.
42. Scheele CW. Om Frucht- och Bär-syran, Kong. Vetenskaps Acad Nya Handlingar. 1785;6:17-27.
43. Scheele CW. Försök Beträffande det Färgande Amnet uti Berlinerblå, Kong Vetenskaps Acad Nya Handlingar; 1782;3:264-275, 1783;4:33-43.
44. Scheele CW. Rön Beträffande et Särskilt Socker-ämne uti Exprimerade Oljor och Fettmor, Kong Vetenskaps Acad Nya Handlingar. 1783;4:324-329.
45. Chevreul ME. Recherches Chimiques sur Plusieurs Corps Gras et Particulièrement sur Leurs Combinaisons Avec les Alkalis, Ann Chim. 1815;94:113-144.
46. Richet, G., The Chemistry of Urinary Stones Around 1800; A First in Clinical Chemistry, Kidney International. 1995;48:876-886.
47. Scheele CW. Undersökningar on Blåsestenen, Kong Vetenskaps Acad Handlingar. 1776;37:327-332.
48. Fourcroy AF, Vauquelin N. Mémoire Pour Servir à l'Histoire Naturelle, Chimique et Médicale de l'Urine Humaine, Contenant Quelques Faits Nouveaux sur son Analyse et son Altération Spontanée, Ann Chim. 1799;31:48-71.
49. Fourcroy AF, Vauquelin N. Mémoire Pour Servir à l'Histoire Naturelle, Chimique et Médicale de l'Urine Humaine, Contenant Quelques Faits Nouveaux sur son Analyse et son Altération Spontanée, Ann Chim. 1799;32:80-162.